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Pilot-scale Experimental Work on Sustainable Process Method of Production of Precipitated Calcium Carbonate from Steel Slag and Carbon Dioxide

Final Project

Department of Energy Engineering and Environmental Protection

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Abstract of master's thesis

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Abstract

Steel is the most manufactured metal in the world, last year 1665 million tones were produced. What is more, in the last decades steel production has increased exponentially. Apart from being the most important metal in industry, it is a major source of carbon dioxide emissions, waste and energy consumption. In a world who is more concerned about global warming each day, trying to reduce greenhouse gas emissions, it is necessary to try to find ways to reduce these emissions. The production of steel generates steel slag, a by-product that can be utilized in industry due to its high calcium content, avoiding then the need of sending it to landfill. Slag2PCC is a process in which is possible to use the steel slag to convert it to precipitated calcium carbonate (PCC). Carbon dioxide flows are used in the process, meaning that it is a way to reduce carbon dioxide emissions and at the same time to reduce energy waste. This is done in two stages: precipitation and carbonation. Precipitation has been studied thoroughly, so carbonation has been the aim of the study.

Tests have been done both in the pilot scale plant and in a laboratory, in order to obtain a specific crystal morphology of PCC, scalenohedral form of calcite. When performing the tests in the pilot plant scale it was not produced scalenohedral, we performed tests in laboratory scale. This could reduce time and money, as reactor in the laboratory scale was 5 L and in the laboratory scale was 200 L. Different tests were done varying carbon dioxide flow used and the quantity of solution flow entering and leaving the reactor.

Cost of producing PCC was estimated as 581.83 €/ton PCC produced based on the parameters utilized in the pilot plant scale. This price is in range of expected if we consider the pilot plant scale as a big scale process.

Keywords steel slag, PCC, carbonation, carbon dioxide, ammonium chloride

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Abbreviations

BF	Blast Furnace
BOF	Basic Oxygen Furnace
CCSP	Carbon Capture and Storage Program
CLEEN	Cluster for Energy and Environment
EAF	Electric Arc Furnace
EDTA	Ethylenediaminetetraacetic acid
GCC	Ground Calcium Carbonate
$GtCO_2$	Giga-tons of Carbon Dioxide
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
kWh	Kilowatt hour
PCC	Precipitated Calcium Carbonate
PVC	Polyvinil chloride
slag2PCC	slag to PCC
SEM	Scanning electron microscope
SLR	Solid to Liquid Ratio
TAPPI	Technical Association of the Pulp and Paper Industry
wt	weight

Symbols

c	concentration of a solute (g/L)
Δc	absolute supersaturation (M, mol/L)
Cp	Specific heat capacity (kJ/kg*ºC)
D	Diffusivity (m^2/s)
G	Growth rate
ΔH	enthalpy (KJ/mol)
k	reaction rate constant (mol/L*atm, L/mol*s, 1/s); mass transfer coefficient (m/s)
m	mass (g, kg)
M	mol/L
M€	million euro
P	Partial pressure (bar, Pa)
Q	heat (kJ/kg)
V	volume (liters)
X	mass fraction
[-]	concentration (M, mol/L)
>>	much greather than
µ	micro (10^{-6})
η	efficiency
σ	relative supersaturation
α	volume shape factor
β	surface shape factor

Subscripts

H	Henry’s Law constant
s	solid
g	gaseous
l	liquid
aq	aqueous
ext	extraction

Superscripts

o	initial
+	cation
-	anion
*	equilibrium

1. Introduction

Nowadays it is important to look for methods that permit the capture and the storage of carbon dioxide in order to reduce the greenhouse gas emissions and to avoid the global warming. One good way to make this possible for example is to try to reduce the waste generated by energy-intensive industries. One of the industries that generate such a large quantity of waste is the steel industry. Steel is the most manufactured metal, in the following figure it is possible to see the evolution of the steel production:

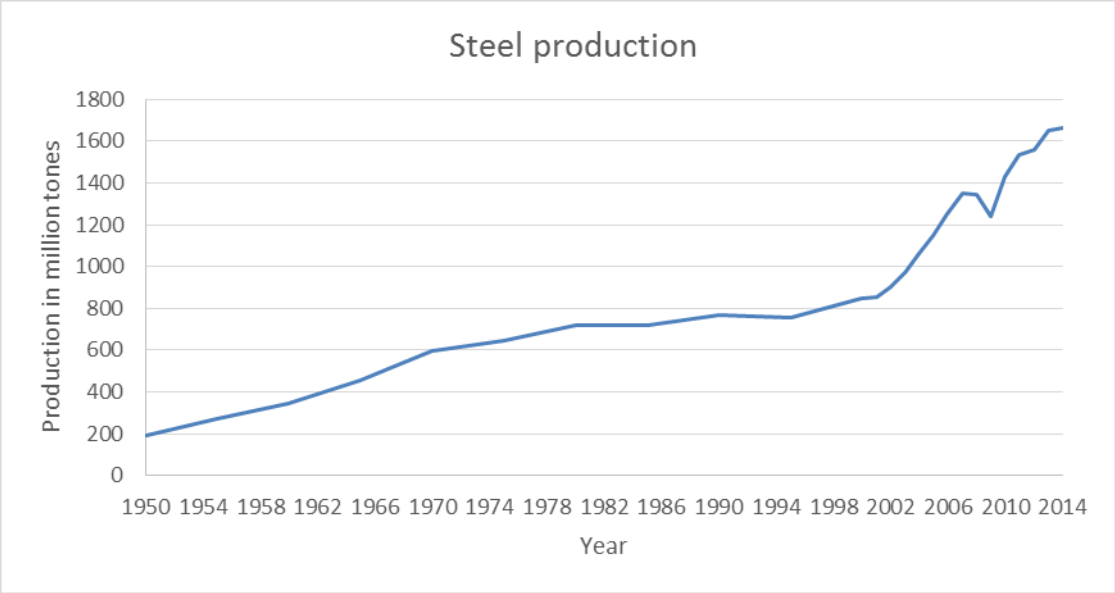

Figure 1.1: Steel Production (WorldSteel, 2015)

It can be easily appreciated that over the years the production of the steel rises each year, last year was exactly 1665 million tones and in 1950 was 189 million tones. It is a very significant growth in only 55 years and the tendency reveals that the production will continue rising: more and more emissions will release to the atmosphere each year. It is very important then to look for methods to capture carbon dioxide emissions.

The emissions of manufacturing steel were estimated at 2.6 $GtCO_2$ in 2006 (both direct and indirect emissions) (III, 2014). Particularly in Finland the production is between 3.5 million tons and 4 million tons each year (Finland, 2014) and the emissions of carbon dioxide from iron and steel industry are approximately 3 million tons each year (Finland, 2013). Apart from the emissions generated by this industry, there is also another concern: the waste produced. Steel industry is a very energy intensive process and it generates a large quantity of waste by-products called slag. In order to reduce the carbon dioxide emissions, to reduce the waste generated and to recycle the calcium, it has been studied over the years to produce precipitated calcium carbonate (PCC) from steelmaking slag.

The process to make this possible is called slag2PCC and it permits to convert the steel slag and carbon dioxide into precipitated calcium carbonate. As the steel slag has very high calcium content,

it is a perfectly suitable material for this process. In the slag2PCC, a solvent is used to extract the calcium from steelmaking slag. In particular ammonium chloride (NH_4Cl) will be used. Then the calcium rich-solution is bubbled with gaseous carbon dioxide which reacts to form PCC. Depending on the PCC particle quality and if the PCC fulfills several requirements, PCC could be used for plastics, paints, paper, construction and for pharmaceutical and chemical industry. In Finland, the main industry that uses PCC is the pulp and paper industry but as the quality requirements for this industry have been studied before in the Energy Engineering and Environmental Protection department, this thesis will focus on the quality requirements for Plastics and Pharmaceuticals.

Slag2PCC project is part from a research program with the name Carbon Capture and Storage Program (CCSP). This program is managed by CLEEN Ltd, (Cluster for Energy and Environment) and its key objective is to develop carbon capture and storage technologies. CCS Program runs from 2011 to 2015 with an approximately budget of 3 M€. Nowadays CCS Consortium consists of 18 industrial partners and 9 research partners being Aalto University one of them.

2. Theory

2.1. Steelmaking slag

Steel industry generates undesired compounds as slag. Slag is produced when the molten steel is separated from impurities in steel-making furnaces and it can be made in integrated steel plants using a BOF, by utilizing a BF or in special steel plants using an EAF. In the case of the blast furnace, 1.025 billion tons of steel with this process were produced in 2010 and around 260-270 kg/ton of slag (Zulhan, 2013). The quantity of steel produced by BOF is approximately 988.6 million tons and by EAF is 410.7 million tons. Then the slag produced in both processes is 12.5% of the steel used, resulting in 174.91 million tons produced. Below it is shown the steelmaking slag process simplified.

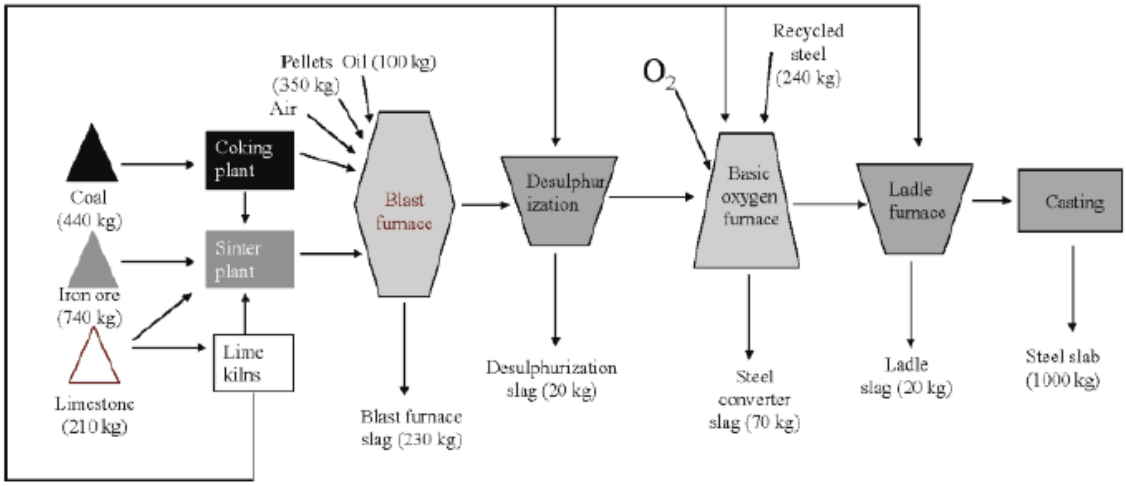

Figure 2.1: Steel Production process diagram (Sanni Eloneva, 2008)

Depending on the stage of the steel making process different types of slag are produced, they differ in chemical composition of the elements. The processes BOF and EAF are normally known as steel slag, therefore only the data referring to this term will be shown. Table 2.1 shows slag composition differences between different processes.

Constituent	Blast furnace slag (%)	Steel slag (%)
CaO	35-42	35-45
SiO2	33-38	11-17
Al2O3	10-15	1-6
MgO	7-12	2-9
FeO	<1.0	16-26
MnO	<1.0	2-6
P_2O_5	-	1-2
S_{total}	1-1.5	<0.2
Cr_2O3	<0.1	0.5-2

Table 2-1: Chemical Composition of PCC products by process (%) (Euroslag, ei pvm)

As it is shown in the table 2.1, the primary components of both slags are calcium oxide (CaO) and silica (SiO_2) because they are produced from lime and silica based melts. The main difference between them is the content of iron (Fe): in blast furnace slag is usually about 0.5% of the total chemical composition and steel slag has a composition of Fe0 of about 16-26% of the total composition. This is because the steel slag is generated by an oxidizing process and therefore the iron content is higher and this is why the steel slag is also known as black slag. Blast furnace slag normally consists of melilite ($Ca_2MgSi_2O_7$- $Ca_2Al_2SiO_7$) and merwinite (Ca_3MgSiO_8) and steel slag consists principally of dicalciumsilicate (Ca_2SiO_4), dicalciumferrite ($Ca_2Fe_2O_5$) and wuestite ($Fe_{1-x-y},Mg_x,Mn_y)O_z$.

The figures 2.2 and 2.3 below shows the currently uses for blast furnace slag and steel slag in 2010:

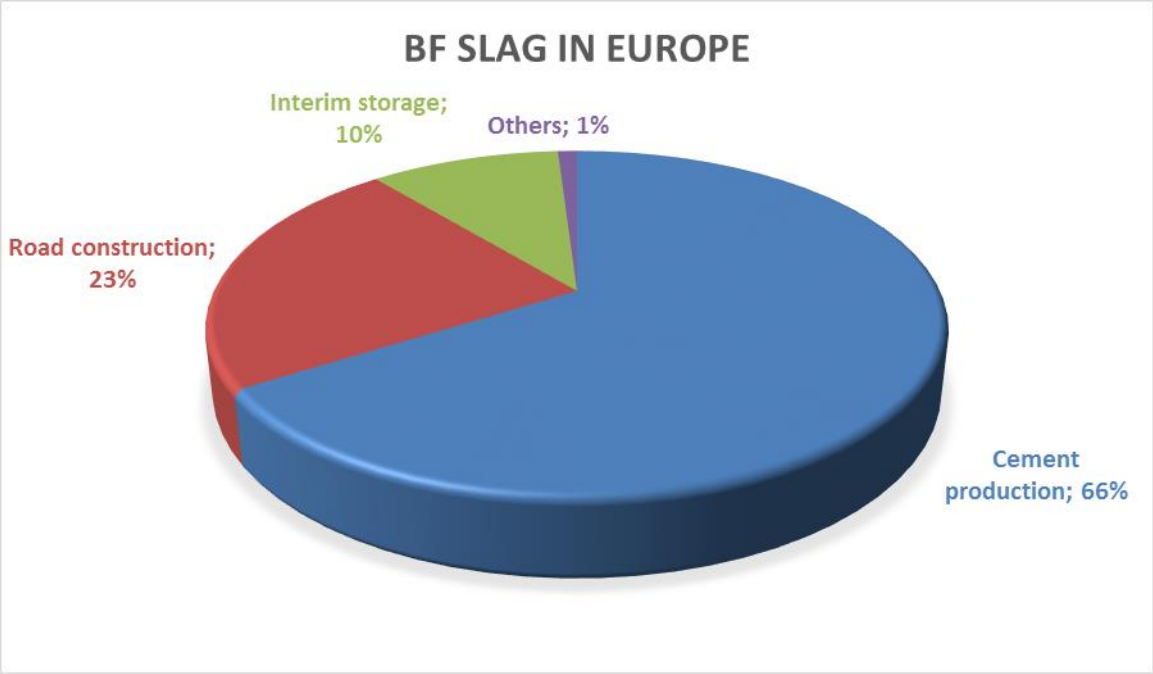

Figure 2.2: Blast furnace slag uses in Europe in 2010 (%) (Zulhan, 2013)

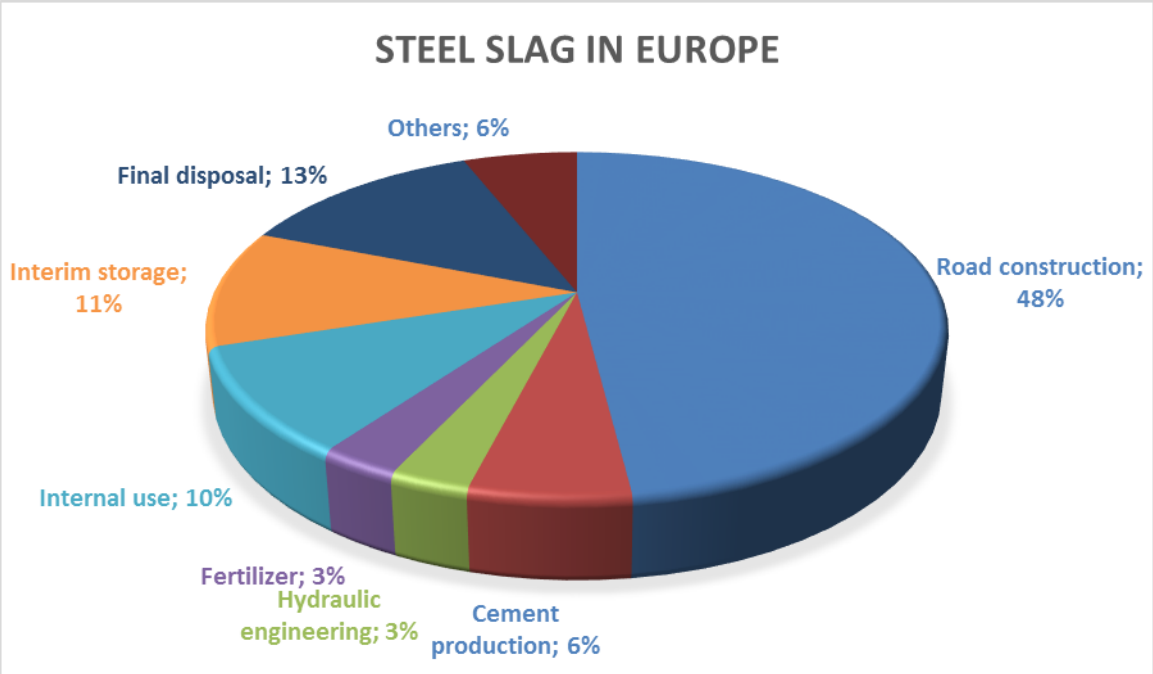

Figure 2.3: Steel slag uses in Europe in 2010 (%) (Zulhan, 2013)

Blast furnace slag is mainly used for cement production and for road construction. The slag used for cement production is produced by granulation technique, whereas the slag used for road construction is basically a crystal form produced from slow cooling process on air. Due to cement production is a process which produces indirect and direct carbon dioxide emissions, with its utilization emissions can be reduced. What is more, it is possible to prevent the soil contamination and air pollution produced by disposing the slag in a landfill.

On the other hand, steel slag is not as utilized in cement production and road construction as BF slag. Another difference is that in the case for steel slag some of the slag is not used, about a 13% of it. Currently some technologies are being studied in order to not waste this percentage of the slag, for example the one that this thesis is about: the production of precipitated calcium carbonate (PCC) from steel slag.

2.2. Calcium Carbonate

Calcium carbonate is a chemical compound with the formula $CaCO_3$ and it is also an abundant mineral found in the nature (Pao-Chi Chen, 1997). It precipitates in three different crystalline forms: calcite, aragonite and vaterite and it is a complex process due to the fact that the operation variables (pH of solution, solution composition, temperature and ionic strength) are interrelated and interact on each other in a crystallization process (J Rohleder, 2001). Calcite is the most thermodynamically stable structure in normal atmospheric conditions whilst aragonite and vaterite are metastable polymorphs that will convert to calcite over geological time (S.R Shirsath, 2015). Calcite crystallizes in the hexagonal-rhombohedral system and as it is the most stable structure, more than 300 hundred forms of calcite have been described (cubical, rhombohedral… etc) (D. Chakraborty, 1994). On the other hand aragonite crystallizes in the orthorhombic system and is commonly found as needle-shaped.

Finally, vaterite belongs to the hexagonal system and it is mostly found as spherulitic or disc-shaped crystals. Only calcite and aragonite are produced on an industrial scale because vaterite is extremely unstable, it just occurs exceptionally in nature (J Rohleder, 2001). Below the figure 2.4 shows the typical forms of calcite, vaterite and aragonite.

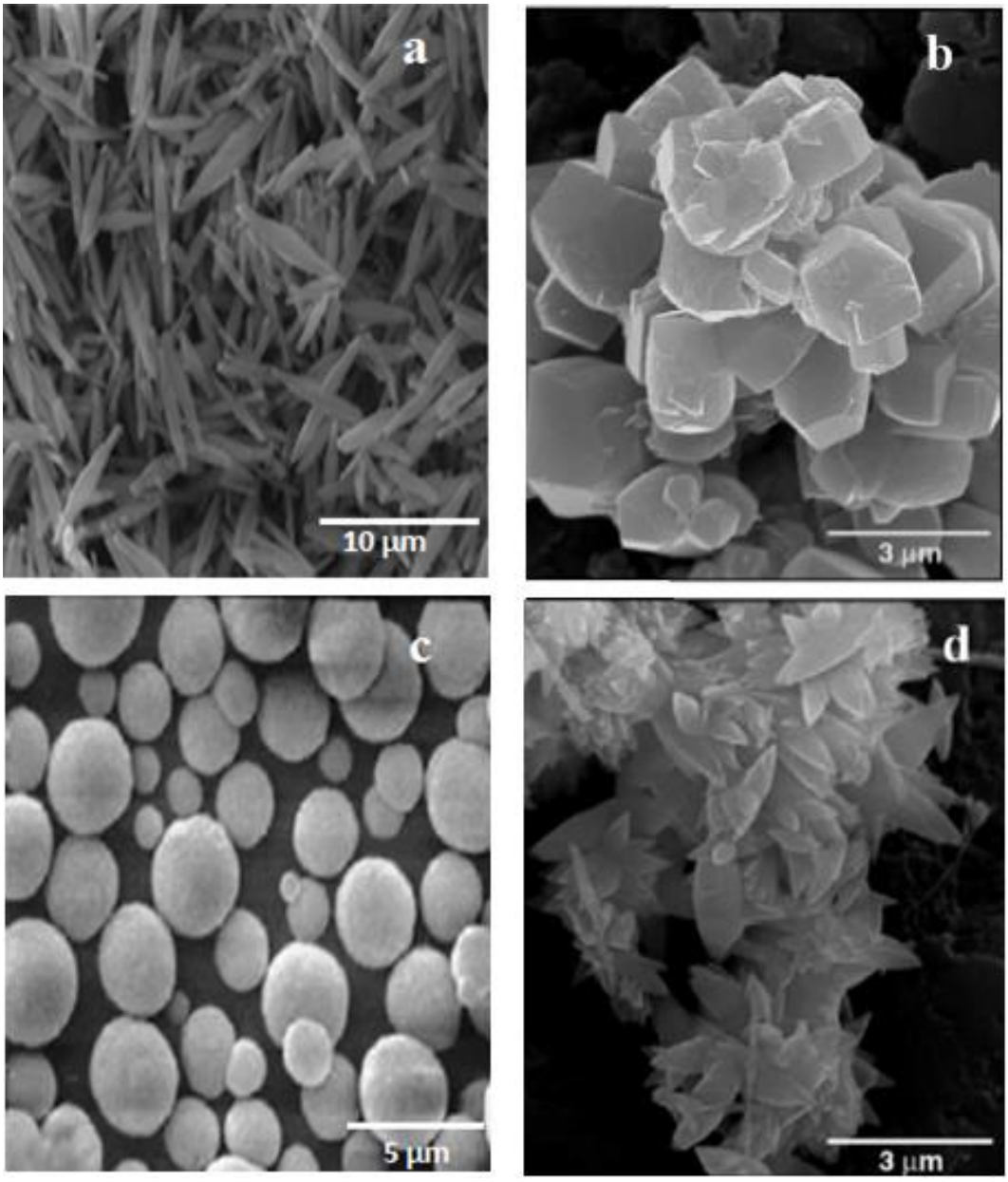

Figure 2.4: SEM of different grades of PCC

a) Aragonite PCC (Gen-Tao Zhou, 2004)
b) Rhombohedral Calcite PCC (Jesús García Carmona, 2003)
c) Vaterite PCC (Andreassen, 2005)
d) Scalenohedral Calcite PCC (Jesús García Carmona, 2003)

Calcium carbonate is a widely used mineral in industry. The industrially important source rocks, with very high calcium carbonate content, are limestone chalk and dolomite (The Essential Chemical Industry online, ei pvm). The most common source is limestone, it consists principally of calcium carbonate and magnesium carbonate ($MgCO_3$) as a secondary component. Limestone deposits are

distributed widely throughout the world, but only a 15% of the limestone in the world is used for chemical and industries applications, such as to make precipitated calcium carbonate (The Essential Chemical Industry online, ei pvm). Most of the limestone is used in metallurgy (60%) and the rest is utilized in construction (25%). The reasons why only a few percentage of the limestone is for making calcium carbonate are that is not always feasible and there are not many calcium carbonate deposits with enough quality to sell to the industry. The quality requirements are purity, degree of whiteness, thickness and homogeneity, and all of them have to be acceptable in order to be feasible the mining process (IMA Europe, ei pvm). When the mineral is extracted then it is crushed, milled, dried and screened in order to produce natural calcium carbonate, or as it is commonly known, ground calcium carbonate (GCC).

If a higher purity is requested for some applications, calcium carbonate has to be produced synthetically by direct carbonation of hydrated lime (Minerals Technologies Specialty Minerals, ei pvm). The process is controlled to assure the right size, uniformity, shape surface area and surface chemistry. The production of PCC permits to grow crystals of different shapes that are not possible to get with GCC such as clustered needles, prims, cubes and rhombohedrons. These crystals have better physical properties which are needed in some applications where GCC cannot fulfill the requirements. PCC can be sold with a higher price than GCC as the process to obtain PCC is more complex. It is shown below the approximate prices at which GCC and PCC can be sold. The price in euros is calculated at the exchange rate of 11st of May 2015.

	Price (£/ton)	**Price (€/ton)**
GCC, coated, fine grade, ex-works	80 – 103	111.8 - 143.9
PCC, coated, ex-works	370 - 550	517 - 768.5
PCC, uncoated, ex-works	340 - 550	475 - 768.5

Table 2-2: Approximate prices for GCC and PCC (Industrial Minerals, 2011)

2.3. PCC Production Technologies

Currently, there are several methods to produce PCC, although not all of them are equally utilized because of their different production costs or workability. The different processes to produce precipitated calcium carbonate are (Stratton, s.f.):

- Carbonation process
- Solvay process
- Lime-soda process
- Calcitech process
- Filler recycling process

The most important methods are carbonation, lime-soda and solvay process because they are the only ones who are used in an industrial scale. Below are described briefly all the technologies in which PCC can be produced.

2.3.1. Carbonation process

This is the only process in which PCC is produced PCC as a primary product. It is the process which is used most frequently, and it is also the simplest and the most cost-efficient production method for PCC (H.P Matilla, 2014). In the carbonation process the calcium carbonate ($CaCO_3$) is calcined in a lime kiln at a temperature between 900 ºC and 1000 ºC, producing calcium oxide (CaO) or as it is also known, quicklime (Stratton, s.f.), due to the high temperature. Then, the calcium oxide is slaked with water and this produces calcium hydroxide ($Ca(OH)_2$). When this waste gas is purified the solution reacts in a tank with the carbon dioxide that contains, causing that the calcium carbonate precipitates. Finally, this precipitate is screened in order to remove the unreacted calcium hydroxide and dried with a filter press and a dryer. A high grade limestone is required (Stratton, s.f.) due to this sort of limestone has the highest content in calcium carbonate.

The reactions that occur in the carbonation process are the ones as follows (H.P Matilla, 2014):

$$CaCO_3(s) \overset{heat}{\longleftrightarrow} CaO\ (s) + CO_2(g)\ (\Delta H = 163\ kJ/mol\ at\ 1000\ ^{o}C) \quad (2.1)$$

$$CaO\ (s) + H_2O\ (l) \leftrightarrow Ca\ (OH)_2\ (s)\ (\Delta H = -65\ kJ/mol\ at\ 20\ ^{o}C) \quad (2.2)$$

$$Ca\ (OH)_2\ (s) + CO_2(g) \leftrightarrow CaCO_3(s) + H_2O\ (l)\ (\Delta H = -113\ kJ/mol\ at\ 20\ ^{o}C) \quad (2.3)$$

2.3.2. Solvay process

In this process sodium carbonate (Na_2CO_3) and calcium chloride ($CaCl_2$) react to form calcium carbonate ($CaCO_3$) and sodium chloride (NaCl). This reaction can be represented with the following equation:

$$NaCl + CaCO_3 \leftrightarrow Na_2CO_3 + CaCl_2 \quad (2.4)$$

Solvay process is less used than carbonation process due to the lower costs of carbonation, and also because with the solvay process the PCC has more impurities. Apart from magnesium carbonate, solvay PCC has gypsum and sodium chloride as well.

2.3.3. Lime-soda process

With lime-soda process is also possible to produce PCC. In this case raw materials are calcium hydroxide ($Ca(OH)_2$) and sodium carbonate (Na_2CO_3) and the final products due to that reaction are sodium hydroxide (NaOH) and calcium carbonate ($CaCO_3$) . The reaction can be represented as:

$$Ca(OH)_2 + Na_2CO_3 \leftrightarrow NaOH + CaCO_3 \quad (2.5)$$

With this process the final product has also impurities, like gypsum, and this is why its use has some limitations, the resulting calcium carbonate has usually poor quality. It has been investigated methods to improve the purity of the PCC, as this method is frequently used to produce NaOH. This process is only feasible by increasing the quality of the PCC (H.P Matilla, 2014).

As these three processes are different, the final PCC produced is different as well. In the table below are shown the different chemical compositions of the PCC by the process used. One thing that can be easily appreciated is that there are no NaCl impurities in the carbonation and the lime-soda processes, they are only present in the solvay process. This is probably because one of the raw materials to produce the PCC in solvay is NaCl and in the other two processes the raw materials do not contain chlorine.

Compound	Carbonation	Solvay	Lime-soda
CaCO3	98.36	98.62	98.43
CaSO4	0.08	0.63	0.78
MgCO3	0.7	0.21	0.37
Al2O3	0.09	0.01	0.07
Fe2O3	0.07	0.01	0.06
SiO2	0.1	0.02	0.04
NaCl	0	0.1	0
% H2O loss (at 110 ˚C)	0.6	0.3	0.25
pH (saturated solution)	9.4	8.5	10.3

Table 2-3: Chemical composition of PCC products by process (%) (Stratton, s.f.)

2.3.4. Calcitech process

PCC in calcitech process is produced by dissolving the calcium into an aqueous solution from a raw material. Practically any material with a significant content of precipitated calcium carbonate can be a raw material, including inferior, by-product and waste raw materials. When the calcium is dissolved the insoluble materials have to be separated and after that calcium precipitates with carbon dioxide in a reactor. Then, the product is passed through a press filter and washed. Finally, depending on the final use, the product is dewatered to obtain 72% of solids slurry (for paper coating) or is dewatered to obtain 99.8% of solid via drying and milling (for plastics and pharmaceutical products).

2.3.5. Filler recycling processes

In the filler recycling process the raw material which the PCC is formed from is paper sludge (H.P Matilla, 2014). Sludge is normally dewatered and then is incinerated or disposed in a landfill. This sludge contains water and calcium carbonate in its third part of dry content (Resource Management Agency, s.f.). It has been studied in the European Union SERECARB (Selective Recovery of Calcium Carbonate) project that is possible to recover selectively the calcium carbonate and to use it as a filler (Resource Management Agency, s.f.).

2.4. PCC applications

Precipitated Calcium Carbonate is used in many industries as filler and to improve some characteristics of the products such as whiteness, UV resistance, abrasivity and rheology (European Commission, 2007). In the case of adhesives and sealants, construction and plastics applications PCC can be coated with a low percentage of fatty acid or other organic material if they are used in non-aqueous systems and in particular coating improves impact strength in plastics (Cales de Llierca, S.A., s.f.).

Below it is shown the PCC global consumption:

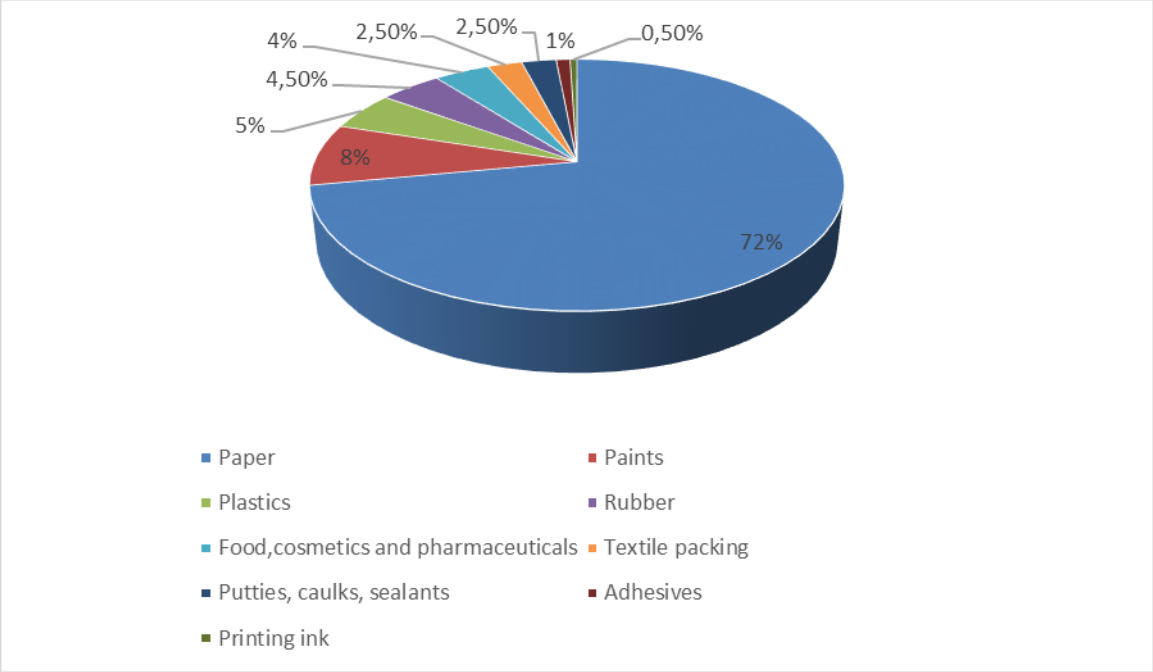

Figure 2.5: PCC World Consumption by industry (Tidco, 2015)

To continue with the applications of PCC, below there are briefly explained all the applications although a further analysis is going to be made in the case of plastics and pharmaceutical industry: utilization, quality requirements, etc.

PCC applications are:

2.4.1. Paper

Paper industry is the industry in which PCC is most frequently used, around 70% of the total PCC is consumed by this industry (Yamuna Calcium Pvt. Ltd., s.f.). PCC is used as filler and improves brightness, smoothness, opacity of paper and increases the ink receptivity. Furthermore, when PCC is used reduces the cost in paper production because less time and energy is required to dry the paper.

2.4.2. Paints and coatings

PCC is used in paints and coatings because it provides high brightness and due to its high whiteness the processability characteristics of paints are improved. Furthermore precipitated calcium carbonate is a setting and opacifying agent, allowing the paint characteristics are more stable and it is also an anti-rust agent (CalciTech Synthetic Minerals Europe, s.f.). It is also a titanium dioxide extender and this permits to reduce the volume of the pigment as well as to reduce the cost of the product (Yamuna Calcium Pvt. Ltd., s.f.)

2.4.3. Plastics

The utilization of PCC in plastics improves strength and toughness as well as the appearance of the final product (whiteness, gloss, surface finish). As mentioned before, coated PCC improves impact strength especially in plastics (CalciTech Synthetic Minerals Europe, s.f.).

2.4.4. Pharma and Food Industry

PCC is used in pharmaceutical applications as an excipient or it can be combined with other excipients. Furthermore the pharmaceutical industries also use PCC to neutralize acids in fermentation processes and for calcium supplement tablets (Yamuna Calcium Pvt. Ltd., s.f.).

2.4.5. Adhesives and sealants

As the particle size of the PCC is narrow, this gives optimum mechanical and rheological properties. Furthermore, it enhances formulation flexibility allowing an increase in filler loading (CalciTech Synthetic Minerals Europe, s.f.). It is also used to neutralize the acids in the fermentation process and for calcium tablets.

2.4.6. Inks

Ink industry uses PCC as a settling agent and thanks to this it is possible to control the strength and body of the ink (Yamuna Calcium Pvt. Ltd., s.f.). PCC is used when a high quality letter press and high quality ink is required.

2.4.7. Rubbers

PCC is used in rubber industry because of its high whiteness and dispensability improves the process ability characteristics of all rubber products. PCC is an excellent filler for rubbers and reduces the final manufacturing cost (CalciTech Synthetic Minerals Europe, s.f.).

2.5. Use of PCC in Plastic Industry

PCC is basically used in the plastic industry as inorganic filler, with its utilization is possible to reduce the cost of producing some thermoplastics and thermosets and permits to improve mechanical properties (Xanthos, 2005). PCC is also used to improve impact resistance, surface gloss, weather ability, shrinkage control, cold flow properties, low and high temperature properties, dielectric properties, and to reduce plasticizer migration and crazing of molded parts (Ciullo, 1996). PCC is

most common used in rigid and flexible PVC and PVC plastisols but also in polyurethane foam, epoxies and phenolic resins.

Although the industry that consumes more PCC is the paper industry, Plastic industry is also a very important consumer of PCC. In 2011 the consumption of calcium carbonate for plastics was 19.3 million tons but only 3.8 million tons were PCC (Chul Seoung Baek, 2014). Ground calcium carbonate is much more consumed than PCC because GCC is less expensive, but PCC has higher purity and whiteness index and it is possible to adjust particle size and shape (Chul Seoung Baek, 2014).

Table 4 shows a comparison of the characteristics between PCC and GCC:

Type	**Calcite PCC**		**Aragonite PCC**	**GCC**	
	Rhombohedral	Scalenohedral	Orthorhombic	Fine	Ultrafine
Refractive index	1.58	1.58	1.63	1.58	1.58
Specific gravity	2.71	2.71	2.92	2.71	2.71
TAPPI brightness (%)	99	99	99	95	95
Surface area (m^2/g)	6 - 8	9 – 15	9 - 13	5 – 7	10 - 12
Einlehner abrasion (mg)	3	3 – 5	4 - 8	8	4
Particle size					
+5 µm (%)		2	3	20	3
-2 µm (%)	99	45	75	70	90
Mean (µm)	0.7	1.0 - 3.0	0.5 -1.0	2	0.8

Table 2-4: Characteristics of PCC and GCC fillers (%) (Chul Seoung Baek, 2014)

According to these characteristics it is possible to appreciate that PCC has better properties, in general it has smaller grain size, the dispersibility decreases and has higher brightness.

Over the years the demand for environmental-friendly fillers has been growing for plastics in advanced countries. One suitable way to achieve that would be carbon capture storage technologies and this is why PCC is really interesting for plastic industry. In particular, in the automotive plastics market the use of PCC has grown because it reduces environmental load. For example, PCC fillers can reduce vehicle weight by about 20% or 10-12 g/km (Chul Seoung Baek, 2014). In terms of carbon dioxide emissions, this is the 5% of the average emissions or 150-200 g/km.

As commented before, PCC is widely used in many different industries, but the quality requirements when is used in a specific application are not the same. For example, in paper industry the quality requirements are that the crystal morphology has to be calcite, they have to have at least 97% of brightness, the particle size should be between 3 and 5 µm (Yamuna Calcium Pvt. Ltd., s.f.). In the case of plastics it will be described particle size, substitution ratio and biodegradability.

2.5.1. Particle size

When PCC is used in plastic it is desired a small grain size, because the smaller the grain size is, the higher the strength becomes. Nevertheless, it does not have to be too small because otherwise the strength decreases. If it is homogeneous PCC with a small grain size it is possible to obtain high viscosity, due to the smaller is the grain size, the higher specific surface area becomes, and as the chemical bonding is then increased, the viscosity increases. The higher the viscosity is, the more strength and durability it can be obtained. So, the size and binding power of the inorganic filler are important, as well as the distance between inorganic filler particle surfaces (Z. Bartcazk, 1999). The distance between the surfaces of the particles should be at least 0,035 µm, otherwise the strength theoretically decreases. Moreover, the particles should be more or less regular in terms of size because if they are not cracks may occur.

2.5.2. Substitution ratio

There is an optimum percentage of filler substitution in plastics: if the polymer is substitute by up to 30% of the polymer weight the elasticity modulus increases, and yield stress and strain decreases. However, the opposite effect occurs if the replacement is below 30% of the polymer weight. As a conclusion, it can be said that the appropriate substitution ratio depends on the molecular weight and particle size of the filler. So, there is a minimum in the optimal substitution ratio but there is also a maximum because adding PCC in the polymer means also that ductility and toughness decrease. Thus, there must be a balance between resistant and deformable material properties. In Figure 7 it is shown the variation in yield strength and the modulus versus percentage of PCC filler used.

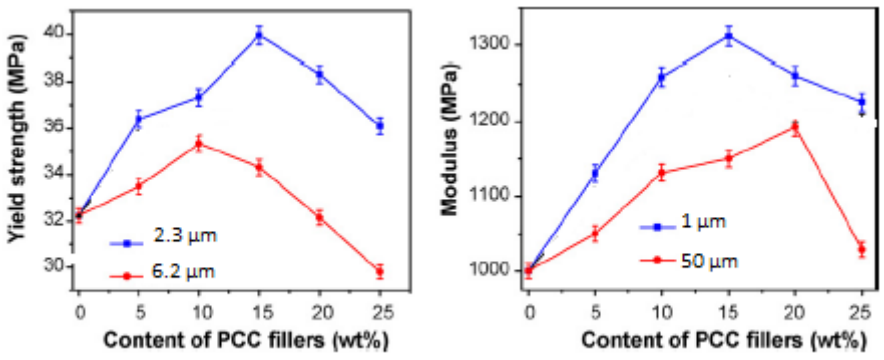

Figure 2.6: Variation on the yield strength and Young's modulus with PCC content (Tran Dai Lam, 2009)

2.5.3. Biodegradability

The use of PCC improves biodegradability as well as physical properties such as bio-plastic strength. When PCC is mixed with biodegradable plastic the polymer disintegrates faster. Plastic decomposition occurs when ultraviolet rays form holes by decomposition of the light-sensitive period. Then, the water can get inside the plastic and this causes the dissolution of PCC. As a final results cracks occur faster and then the microorganisms infiltrate. It has been studied by Baek (Chul Seoung Baek, 2014) that when the grain size is 0.04 µm the strain at break is improved at maximum and the decomposition rate is increased a 60 wt% with calcium carbonate.

2.6. PCC utilization in Pharmaceutical Industry

Most common use for PCC in pharmaceutical industry is as an antacid, but it is also used as a calcium source, as a neutralization and filtration aid in antibiotic manufacture, as a buffering and dissolution aid in soluble tablets, as a bulking agent in tableting and as a calcium supplement (Tidco, 2015). PCC is used in this industry because is a fast and effective acid neutralizer, it has a very high absorptive power and it is less expensive than other fillers and extenders. When PCC is used as an antacid, it can be in several forms: tablets, liquids, soft chews, soft gels, effervescents and chewing gums (Minerals Technologies Specialty Minerals, 17).

2.6.1. Antibiotic manufacture

In the antibiotics manufacture, when they are fermenting PCC is added to control and buffer the pH and after this is added as a flocculant in order to improve the clarification and filtration of the product. For antibiotic manufacture high surface area is specially required because it improves the absorption rate and a high purity of PCC is also required. Regarding the morphology of the crystal, scalenohedral form of calcite is recommended because this crystal gives a high surface area and the particle size normally are from 2 to 3 μm.

2.6.2. Calcium-Based Pharmaceutical Raw Materials

PCC can also be used to manufacture other pharmaceutical products, for example to make a calcium salt and use it for nutritional supplement, for food fortification or can be reacted into a new drug. The quality requirements are more or less the same than in antibiotics: high purity, scalenohedral calcite crystal morphology but the surface area does not have to be as high as in antibiotics.

2.6.3. Buffered aspirin and other buffered tablets

PCC is used to manufacture aspirin and other pharmaceutical products in which their main active component may cause stomachache because of the low pH. It reduces discomfort in the stomach due to the acid neutralizing capacity, when PCC is added in the tablet it helps to stabilize the mixture because of the high pH.

2.6.4. Tablet excipient and filler

When PCC is used as a tablet excipient before utilization it should be first granulated. Furthermore, PCC is an excellent filler as, when moisture is absorbed, hygroscopic ingredients become sticky or clump.

In order to compare the quality requirements between plastic and pharmaceutical industry tables 5 and 6 show chemical and physical properties in both industries:

Chemical properties	Plastic Grade	Pharmaceutical Grade
Color	Bright white	Bright white
Hunter whiteness	97% Min.	97% Min.
$CaCO_3$ % by weight	98.5% Min.	98.5% Min.
Lead as Pb	Traces	Traces
Copper as Cu	Negligible	Negligible
Arsenic as As	NIL	NIL
Sulphate as SO_4	0.01% Max.	0.2% Max.
Soluble alkali as Na2O	0.2% Max.	0.15% Max.
Silica as SiO_2	0.15% Max.	0.07% Max.
Iron as Fe	0.07% Max.	0.01 % Max.
pH	9.0 to 10.5	9.0 to 9.5
Phosphate as PO_4	0.05% Max.	0.05% Max.
Chloride as Cl	Traces	Traces
Magnesium as MgO	0.7% Max.	0.7% Max.
Flouride as F	Traces	Traces
Manganese (Mn)	0.005% Max.	0.005% Max.
Solution in 5N HCl	Clear	Clear
Aluminium, Iron, Phosphate and other matter insoluble in HCl - IS 918/1985	0.5% Max.	0.5% Max.
Typical particle size (µm)	0.8 to 5	0.8 to 5

Table 2-5: Chemical properties in Plastic and Pharmaceutical Grade (Yamuna Calcium Pvt. Ltd., s.f.)

Physical Properties	Plastic Grade	Pharmaceutical Grade
Crystal Structure	Calcitic	Calcitc
Water Absorption	80 to 85 ml/100 mg	50 to 55 ml/100 mg
Oil Absorption	60 to 65 ml/100 mg	30 to 35 ml/100 mg
Loss on Drying at 1050 °C	0.8% Max.	0.8% Max.
Specific Gravity	2.6 to 2.7 Max.	2.65
Bulk Density	0.45 to 0,50 mg/ml	0.60 to 0.70 mg/ml
Average Particle Size	3 to 5 µm	3 to 5 µm
Residue on 300 mess	0.2% Max.	0.2% Max.

Table 2-6: Physical properties in Plastic and Pharmaceutical Grade (Yamuna Calcium Pvt. Ltd., s.f.)

As it can be seen from tables 5 and 6, the chemical properties are almost the same, the only difference between them it is that the maximum pH in pharmaceutical grade is less than in plastic grade. Regarding physical properties, although it is not written in the table, crystal structure are the same but in the case of plastic grade, aragonite calcite is also used and in pharmaceutical grade is only recommended the scalenohedral calcite. Water and oil absorption are better in plastic grade and PCC for pharmaceutical grade is denser than in plastic grade.

2.7. PCC from Steelmaking slag (Slag2PCC process)

Mineral carbonation technology is a process in which carbon dioxide is chemically reacted with calcium or magnesium-materials in order to form stable carbonate materials. This technology is nowadays studied because with its utilization carbon dioxide emissions can be reduced. The carbon dioxide is fixed with calcium or magnesium silicate to produce calcium or magnesium carbonate and silicon dioxide (Arshe Said, 2013). This process is represented by the equation below:

$$(Ca,Mg)Si_2(s) + CO_2 \rightarrow (Ca,Mg)CO_3(s) + SiO_2\ (s) \quad (2.6)$$

Natural deposits of magnesium based silicates are spread throughout the world with huge amounts of them. There are several groups of magnesium silicates and the most found in the world are olivine (Mg,Fe)SiO_4, forsterite ($MgSiO_4$) and serpentine ($Mg_3Si_2O_5$). However, natural deposits for calcium silicates are not that common. The content of magnesium oxide (MgO) in magnesium silicate rocks is higher than the content of calcium oxide in calcium silicate rocks. In particular, magnesium silicate rocks have more than 50% by weight of MgO and calcium silicate rocks 10% by weight (Olajire, 2013). The calcium silicate rock with higher content of MgO is wollastonite ($CaSiO_3$).

Even though there are more magnesium silicate resources in the world the interest in calcium silicates is bigger because of the calcium content. There are several ways to classify the carbonations process. One of them is depending on the steps of the carbonation, direct carbonation if the carbonation occurs in one step, and indirect carbonation if several steps are needed. Another way to classify is if the process use gaseous or aqueous phase. Below, figure number 8 shows a simplified diagram of the direct and the indirect carbonation.

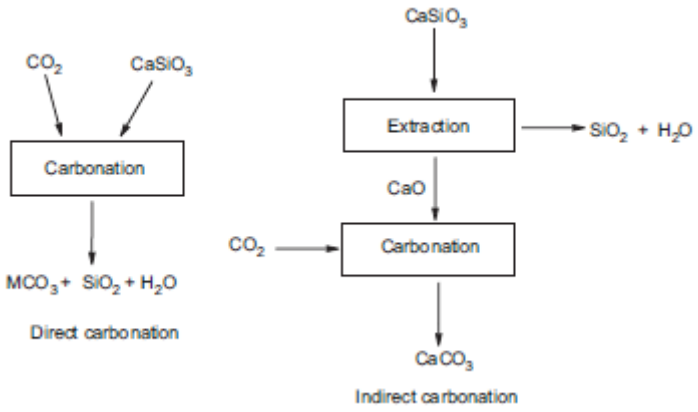

Figure 2.7: Direct and indirect carbonation diagram (Eloneva, 2008)

Direct carbonation is less complex but with the indirect carbonation it is possible to produce a very high purity of calcium carbonate. In fact, this is the carbonation process that a further analysis will be done.

The process to produce precipitated calcium carbonate (PCC) from steelmaking slag is called slag2PCC. This process permits to reduce the CO_2 emissions but it is also possible to recycle the

calcium. Steel slag is used due to its high calcium content. In the process a solvent is used to extract calcium from steelmaking slag, in particular ammonium chloride (NH_4Cl) among other solvents can be used: ammonium nitrate (NH_4NO_3) and ammonium acetate (CH_3COONH_4). Ammonium chloride is selected because it has been the most utilized in previous experiments, it is the cheapest and it has a lower calcium extraction performance (Eloneva, 2008). When finished the slag is removed and then the calcium rich-solution is bubbled with gaseous carbon dioxide which reacts to form PCC. Depending on the PCC particle quality and if the PCC fulfill several requirements, the PCC could be used for plastics, paints, paper, construction, and for pharmaceutical and chemical industry.

Some of the reactions that take place in the calcium extraction are the ones as follows (Mattila, 2014):

$$CaO(s) + 2NH_4Cl + H_2O(l) \rightarrow CaCl_2(aq) + 2NH_4OH\ (aq) \quad \Delta H = -(83 - 88)\ kJ/mol \quad (2.7)$$

$$Ca_2SiO_4(s) + 2NH_4Cl(aq) + H_2O(l) \rightarrow CaCl_2\ (aq) + CaSiO_3(s) + 2NH_4OH(aq)$$

$$\Delta H = -(47 - 52)\ kJ/mol \quad (2.8)$$

And the reactions that describe the carbonation are (Mattila, 2014):

$$2NH_4OH(aq) + CO_2\ (g) \leftrightarrow (NH_4)_2CO_3\ (aq) + H_2O\ (l) \quad \Delta H = -110\ kJ/mol \quad (2.9)$$

$$(NH_4)_2CO_3(aq) + CaCl_2\ (aq) \leftrightarrow CaCO_3(s) + 2NH_4Cl(aq) \quad \Delta H = 14 - 19\ kJ/mol \quad (2.10)$$

When the extraction and carbonations steps are finished, as it is shown in the last equation, final products are the PCC and the ammonium chloride that later NH_4Cl will be recycled. In figure 2.8 the slag2PCC is represented:

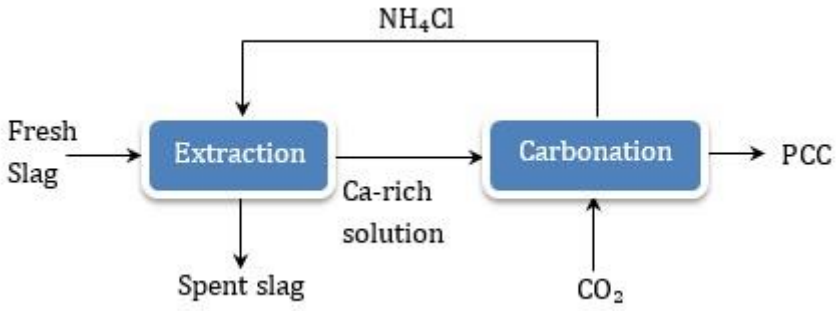

Figure 2.8: Slag2PCC process scheme (Järvinen, 2015)

Regarding to the feasibility of the Slag2PCC Process, it can be seen in a feasibility study made by Eloneva et al (Sanni Eloneva, 2010) that the process is not only feasible, but also it could have benefits. Table 2.8 shows the prices of the possible solvents per tons of carbon dioxide, the price at PCC can be sold and the carbon dioxide emission allowance cost:

	Price (€/t CO_2)
NH_4Cl	26
NH_4NO_3	40
NH_4CH_3COO	40
PCC	227
CO_2	13

Table 2-7: Solvent, PCC and emissions allowance price (Sanni Eloneva, 2010)

As it can be seen from the table, Slag2PCC Process is attractively economical to implement it on an industrial scale. Based on this data if ammonium chloride is used as solvent, it can be said that the benefit is 188 €/ton CO_2 (227-13-26 = 188 €). It has to be taken into account that the prices of the solvent are given based on 5% NH_3 losses/cycle. As the price of the solvent is really important to calculate the feasibility of the process, the solvent losses should be reduced as much as possible.

2.8. Extraction step

It has been commented before that the calcium is selectively extracted from the steel slag. During the extraction step several parameters must be considered to take into account, in this section it is explained slag quality, particle size, solvent (election, concentration and reuse), reaction temperature and properties of the slag residue. For example slag quality is really important, the possible impurities that slag can contain should be removed before carbonation because, otherwise, the final PCC could not be pure enough. In the extraction step it is very important to see if the calcium extraction efficiency ($\eta_{ext,Ca}$) is optimal. This is calculated with the equation shown below:

$$\eta_{ext,Ca} = \frac{C_{ca} * V}{m_{slag} * X_{ca}} \ (\%) \qquad (2.11)$$

Where C_{ca} is the content of calcium expressed in g/l, V is the volume of the solvent used in liters, m_{slag} is the mass of the slag in grams and X_{ca} is the calcium mass fraction in the slag.

2.8.1. Slag quality

Slag composition depends on the steelmaking process and the post-treatment of the slag when formed (Mattila, 2014). One factor that has been studied is that may change extraction efficiency of the calcium is the slag storage placement. When the slag is stored outdoors, extraction efficiency is lower but it is not really significant if we compare it when the slag is stored indoors (H-P. Mattila, 2014). Besides, to use fresh or recycled slag seems to be important in extraction efficiency: when fresh slag is used more extraction efficiency is obtained (Hannu-Petteri Mattila, 2012). The table 2.9 shows the slag fraction composition of the slag used:

CaO	FeO	SiO_2	MnO	Al_2O_3	MgO_2	V_2O_3	Ti	P	Cr	Na_2O
51.4	14.60	13.70	1.80	1.60	1.50	2.05	0.55	0.45	0.25	0.1

Table 2-8: Slag fraction composition

The slag that when used produces best extraction efficiency is the slag with a high free lime content, so with this slag it is possible to obtain a proper extraction efficiency as this slag contains a 51.4% of free lime content.

2.8.2. Particle size

As Said et Al. demonstrated in a study (Arshe Said, 2013), particle size has a significant effect in calcium extraction efficiency. It was studied the percentage of the calcium extracted with three different grain sizes of slag (0-125, 250-500 and 0-1000 μm). It was proved that the smaller the steel converter slag grain size is, the larger the surface area. Consequently, the mass transfer rate will be better and the calcium extraction efficiency higher. This means that it may be necessary the grinding of the material to obtain smaller grain sizes to improve the extraction efficiency. So, the better extraction efficiency was obtained with the smallest slag (0-125 μm). The solvent used was NH_4Cl 1M with a solid to liquid ratio of 20 g/l.

2.8.3. Chosen solvent, concentration and reuse

As it was commented before, ammonium chloride (NH_4Cl) is the most utilized solvent in the slag2PCC process due to it is the cheapest and it has a lower calcium extraction performance. Furthermore, the use of ammonium nitrate (NH_4NO_3) is limited in some countries because it has an explosive nature (Mattila, 2014).

However, in the study made by Said et al. (Arshe Said, 2013), the solvents with better extraction efficiency were ammonium nitrate and ammonium acetate (NH_4CH_3COO).

Eloneva (Eloneva, 2008) also agreed in her experiments that ammonium nitrate and acetate have better extraction efficiency, but she selected first ammonium chloride and acetate. Other solvents were selected as well, for example aluminum nitrate and aluminum sulphate, because they give aqueous solutions that are acidic.

Ammonium chloride, nitrate and chloride were the ones that were selected as suitable solvents, even though they do not have the best extraction efficiency. Ammonium acetate is a salt of weak acid and base but even that the aqueous solution should be neutral, NH_4CH_3COO can dissolve calcium almost as well as NH_4Cl and NH_4NO_3 (with strong acid and weak base). Finally, NH_4Cl was selected as the best solvent for the reasons mentioned before.

Regarding the reuse of the solvent, Mattila et al. (Hannu-Petteri Mattila, 2012) observed that when the solvent is used several times in extraction/carbonation cycles, the reactions are kinetically similar than if the solvent is fresh. Nevertheless, the equilibrium concentrations are slightly different because of the remaining ions from previous cycles.

2.8.4. Solid to liquid ratio (SLR)

Solid to liquid ratio is another important parameter in the extraction step. It is the ratio between the dry waste expressed in grams and the volume of the solvent expressed in liters. This is defined in the following equation:

$$SLR = \frac{m_{slag}\,(g)}{V_{solvent}(l)} \tag{2.12}$$

Said et al. (Arshe Said, 2013) also studied the effect of the solid to liquid ratio in calcium extraction efficiency. They saw doing the experiments that the extraction efficiency was higher when the solid to liquid ratio was low. However, if we decrease the SLR the reactor has to be larger, so this means

that this option might be more expensive. In the experiments one gram of steel converter slag was used, the concentration of the ammonium chloride was 1M and the slag grain size was between 74 and 125 µm.

2.8.5. Reaction temperature

Mattila et al. (Hannu-Petteri Mattila, 2012) observed that the reaction temperature does not have influence on the extraction kinetics. The solvents tested in this study were ammonium chloride and nitrate.

2.8.6. Properties of slag residue

It has been demonstrated in the study made by Mattila et al. (Hannu-Petteri Mattila, 2012) that the chlorine of the ammonium chloride can precipitate on the solid residue. In order to minimize losses of the solvent component a further treatment of the slag seems to be necessary.

2.8.7. Agitation methods

It is considered that the utilization of ultrasound increases the conversion, enhances selectivity and improves the yield (Leigh C. Hagenson, 1998). The effects of ultrasound can be classified into chemical and mechanical. Chemical effects are because of the implosion of microbubbles and mechanical effects because of shock waves during cavitation. Both effects are also known as sonication. Arshe et al. (Arshe Said, 2015) exanimated the effect of agitation methods on extraction efficiency, in particular they compared ultrasonic and mechanical agitation methods. These tests were taken with an aqueous solution of 1 M NH_4Cl, 20 g/l of solid to liquid ratio using sonication and mechanical agitations. The particles sizes were between: (a) 50-74 µm, (b) 74-125 µm, (c) 125-250 µm, (d) 250-500 µm, (e) 500-1000 µm. As it is possible to appreciate, sonication improves greatly calcium extraction efficiency and this effect is even better in the smallest particle size: 96% of the calcium is extracted with sonication and only 65% of the calcium by mechanical agitation.

2.9. Carbonation step

After the extraction step, the precipitation of the PCC via carbonation takes place. Basically in an industrial scale precipitation processes are mostly studied by solid-liquid separation processes in order to obtain a dry product (J. Franke, 1995). Nonetheless, precipitated calcium carbonate is produced by introducing reacting carbon dioxide with lime and this is a gas-liquid-solid reaction, but the subject has not been further studied due to its complexity (Pao-Chi Chen, 1997). To minimize the energy consumption in this process seems to be necessary to control the precipitation by adjusting the reactants concentration (or supersaturation), $[Ca^{2+}]/[CO_3^{2-}]$ ratio and using additives in order to achieve the crystal morphology desired (Özlem Cizer, 2012). Supersaturation determines the nucleation and growth rates of calcium carbonate and it is needed for the precipitation occurs. Furthermore, other requirement qualities have to be fulfilled, for example crystal size, purity, shape… In fact, precipitation process, or crystallization, is a complex process because, as it was commented in previous sections, calcium carbonate can precipitate in three crystalline forms: calcite, aragonite

and vaterite. What is more, the operating variables are interrelated and interact on each other in the crystallization process. These variables are, for example, pH of solution, solution composition, temperature and ionic strength (Pao-Chi Chen, 1997).

In the following sections the factors that affect precipitation and the chemical reactions are discussed.

Overall chemical reactions in the carbonation

As commented before PCC is produced by gas-liquid-solid reaction method. Zappa (Zappa, 2014) gathered in his thesis all the chemical reactions and relevant equilibria in the system. All of them are shown below:

Gas-liquid equilibria

$$CO_{2(g)} \leftrightarrow CO_{2(aq)} \quad (2.13)$$

$$NH_{3(g)} \leftrightarrow NH_{3(aq)} \quad (2.14)$$

$$H_2O_{(g)} \leftrightarrow H_2O_{(l)} \quad (2.15)$$

Liquid phase equilibria

$$CO_{2(aq)} + OH^-{}_{(aq)} \leftrightarrow HCO^-_{3(aq)} \quad (2.16)$$

$$HCO^-_{3(aq)} + OH^-{}_{(aq)} \leftrightarrow CO^{2-}_{3(aq)} + H_2O_{(l)} \quad (2.17)$$

$$CO_{2(aq)} + H_2O_{(aq)} \leftrightarrow H_2CO_{3(aq)} \quad (2.18)$$

$$H^+_{(aq)} + HCO^-_{3(aq)} \leftrightarrow H_2CO_{3(aq)} \quad (2.19)$$

$$H^+_{(aq)} + CO^{2-}_{3(aq)} \leftrightarrow HCO^-_{3(aq)} \quad (2.20)$$

$$Ca^{2+}_{(aq)} + HCO^-_{3(aq)} \leftrightarrow CaHCO^+_{3(aq)} \quad (2.21)$$

$$Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)} \leftrightarrow CaCO^0_{3(aq)} \quad (2.22)$$

$$Ca^{2+}_{(aq)} + OH^-_{(aq)} \leftrightarrow CaOH^+_{(aq)} \quad (2.23)$$

$$Ca^{2+}_{(aq)} + Cl^-_{(aq)} \leftrightarrow CaCl^+_{(aq)} \quad (2.24)$$

$$NH^+_{4(aq)} + HCO^-_{3(aq)} \leftrightarrow NH_4CO_{3(aq)} \quad (2.25)$$

$$NH^+_{4(aq)} + Cl^-_{(aq)} \leftrightarrow NH_4Cl_{(aq)} \quad (2.26)$$

$$NH_{3(aq)} + H^+_{(aq)} \leftrightarrow NH^+_{4(aq)} \quad (2.27)$$

$$\mathrm{NH_{3(aq)} + CO_{2(aq)} \leftrightarrow NH_2COOH_{(aq)}} \quad (2.28)$$

$$NH_2COO^-_{(aq)} + H^+_{(aq)} \leftrightarrow NH_2COOH_{(aq)} \quad (2.29)$$

$$NH_{3(aq)} + HCO^-_{3(aq)} \leftrightarrow NH_2CO^-_{2(aq)} + H_2O_{(aq)}$$
(2.30)

Solid-liquid equilibria

$$Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)} \leftrightarrow CaCO_{3(s)} \quad (2.31)$$

Gas-liquid equilibria equations describe the equilibrium between CO_2 and NH_3, as well as the equilibrium between liquid water and gaseous water. Liquid-phase equilibria equations describe the equilibrium between carbonate species (2.16-2.20), calcium species (2.21-2.24) and ammoniacal and carbamic species (2.25-2.30). Solid-liquid equilibria equation represents the precipitation of calcium carbonate. Some of the components mentioned above are not going to form in a significant way, such as $NH_4Cl_{(aq)}$ and $CaCl^+$.

The main reactions in which CO_2 is absorbed into aqueous $Ca(OH)_2$ solution are represented below (O. Velts, 2011):

Physical dissolution of gaseous CO_2 solution:

$$CO_{2(g)} \leftrightarrow CO_{2(aq)} \quad (2.32)$$

Formation of bicarbonate:

$$CO_{2(aq)} + OH^-_{(aq)} \underset{k_{12}}{\overset{k_{11}}{\rightleftarrows}} HCO^-_{3(aq)} \quad (2.33)$$

Dissociation of bicarbonate:

$$HCO^-_{3(aq)} + OH^-_{(aq)} \underset{k_{22}}{\overset{k_{21}}{\rightleftarrows}} CO^{2-}_{3(aq)} + H_2O_{(l)} \quad (2.34)$$

Ionization of water

$$OH^-_{(aq)} + H^+ \underset{k_{32}}{\overset{k_{31}}{\rightleftarrows}} H_2O_{(aq)} \quad (2.35)$$

CO_2 hydration:

$$CO_{2(aq)} + H_2O_{(aq)} \underset{k_{42}}{\overset{k_{41}}{\rightleftarrows}} HCO^-_{3(aq)} + H^+ \quad (2.36)$$

Formation of the $CaCO_3$ crystals:

$$Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)} \underset{k_{52}}{\overset{k_{51}=\frac{k_{52}*[CaCO_3]_S}{k_{sp}}}{\rightleftarrows}} CaCO_{3(s)} \quad (2.37)$$

Carbon dioxide solubility equilibrium in the equation (2.37) follows Henry's law, at a pressure of maximum 5 atm:

$$[CO_{2(aq)}]_{eq} = k_H * P_{CO_2} \quad (2.38)$$

Where k_H is the Henry's law constant and P_{CO_2} is the CO_2 partial pressure.

It has been studied by Velts et al. (O. Velts, 2011) a modeling procedure in the liquid phase (2.16-2.30). They calculated the values of the reaction rate constants in the equations mentioned before, these results are presented in the following table:

Parameter	Value	Parameter	Value
k_{11}, L/mol*s	$8.4 * 10^3$	k_{41}, s^{-1}	$2.4 * 10^{-2}$
k_{12}, s^{-1}	$2.0 * 10^{-4}$	k_{42}, L/mol*s	$5.7 * 10^4$
k_{21}, L/mol*s	$6.0 * 10^9$	k_H, mol/L*atm	$3.5 * 10^{-2}$
k_{22}, s^{-1}	$1.2 * 10^6$	ρ_{co2}, kg/m^3	1.8
k_{31}, L/mol*s	$1.4 * 10^{-6}$	k_{51}, L/mol*s	$1.88 * 10^6$
k_{32}, mol/L*s	$1.3 * 10^{-3}$	k_{52}, s^{-1}	$9.00 * 10^{-3}$

Table 2-9: Reaction rate constants values O. Velts, 2011

According to these results it can be said that the reactions are really fast looking at the reaction rate constants. Formation of carbonate happens relatively fast and dissociation of bicarbonate and formation of $CaCO_3$ are practically instantaneous.

2.9.1. Factors affecting the precipitation

As precipitation is a complex process most of the studies about PCC precipitation have studied liquid-liquid-solid reactive process because the operation is simpler. For this reason it was difficult to find data about gas-liquid-solid reacting methods. Furthermore, there is no much information about the utilization of the solvent selected for this process, NH_4Cl. Although the conditions are not the same, they do not differ so much from the process we are going to study further, and all the information gathered is useful for the following results and discussion. In the next sections a summary about all the parameters that affect the precipitation of calcium carbonate is shown.

a) Solvent concentration

Mattila et al. (Hannu-Petteri Mattila, 2012) observed that ammonium salt did not affect the kinetics of the carbon reaction. Nonetheless with high solvent concentration (higher than 1.5 M) and high solid to liquid ratio (higher than 100 g/L), the pH of the solution at first decreased but after 20-30 minutes the pH decreased faster, 2 units, and maintained stable. This might be because when the solution has a high ammonia concentration the carbon dioxide absorption is different. In this case the NH_3:NH_4^+ ratio is high and instead of the majority of bicarbonate ions formed, carbamate ($NH_2CO_2^-$) ions will be formed:

$$NH_{3(aq)} + HCO_{3(aq)}^- \leftrightarrow NH_2CO_{2(aq)}^- + H_2O_{(l)} \quad (2.39)$$

In the study done by Cheng et al. (Huaigang Cheng, 2014), it has been tested the effect of the ammonia in the crystal polymorph. They realized the study under the conditions of low concentration of Ca^{2+} (0,015 M) and low degree of supersaturation. The reason why they did with low degree of

supersaturation is because it is easier to control the crystal polymorph. Without ammonia the precipitate of calcium carbonate was mainly calcite (>98%) and a little amount of vaterite. When ammonia was added to the reaction system, the amount of vaterite increased and at the same time aragonite was also formed.

b) Temperature

Temperature has a significant effect in PCC precipitation. Mattila et al. (Hannu-Petteri Mattila, 2012) observed the effect of the temperature comparing the results from experiments at 30°C and 70°C and they noticed that the reaction kinetics is barely affected by the temperature. However, the pH was lower at 70°C than at 30°C. Furthermore, they also noticed that when the temperature of the process was high the gas absorption was poorer and carbon dioxide does not precipitate with calcium. On the contrary, carbon dioxide leaves the reactor in gaseous form. Sun et al. (Yong Sun, 2011) studied the effect of the temperature as well. They observed that with higher temperatures more weight of precipitated mass was obtained. They tested at 20°C, 40°C, 60°C, and 80°C. The maximum obtained was at 60°C, at 80°C the precipitated mass decreased. The solvent used in the extraction was NH_4Cl with a 2M concentration at 60°C (this temperature enhanced the precipitated mass) during 120 min, the solid to liquid ratio was 100 g/l and the sieve sizes were between 38 µm and 250 µm. The carbonation took place with 10 bar of carbon dioxide pressure, 0.37 M of $[Ca^{2+}]$ during 60 min. They observed effects in the crystal morphology as well, when they increased the temperature it changed from scalenohedral at 20°C to rhombohedral morphology. Rhombohedral morphology was more stable below 80°C.

c) pH

Li et al. (Wei Li, 2013) studied the dynamics of calcium carbonate precipitation induced by microbial intracellular or extracellular carbonic anhydrase (CA) at different pH levels (6.0, 6.5, 7.0 and 8.0). The tests took place at 20°C and 1 atm in glass desiccators. Glasses contained 400 ml 0.1 M NH_4HCO_3 solution. They realized the tests with three different systems: system A was a control water system and systems B and C were enzymatic sytems. The initial pHs were set by dilute HCl or NaOH solution. The results showed that pH affected the rate of calcium carbonate precipitation in all of the systems, when the initial pH was in the range from 6.0 to 8.0 the conditions for the precipitation were better. With a high content of OH^- ions carbon dioxide into the solution is enhanced and, therefore, favorable for the precipitation of the $CaCO_3$. Tai et al. (Clifford Y. Tai, 1998) reported that the pH of the solution is the most important factor regarding crystal morphology. They studied how several parameters affected the precipitation with a $CaCl_2/Na_2CO_3$ reacting system. They obtained high-purity calcites at a pH higher than 12 and high-purity vaterites at a pH lower than 10 at room temperature. Maximum yield of aragonite is obtained with a pH 11, and with a high temperature aragonite is the major product with a pH lower than 11 and also presents calcite.

d) Supersaturation

Supersaturation is needed for the precipitation as it was commented before and it is the difference between the concentration of a solute c and the equilibrium value c^*. Rate of crystallization can be expressed by the degree of supersaturation (Mersmann, 2001).This can be expressed with the equation 2.40 (Mersmmann, 1999):

$$\Delta c = (c - c^*) \tag{2.40}$$

It can also be defined the relative supersaturation, σ:

$$\sigma = \frac{\Delta c}{c^*} \tag{2.41}$$

Supersaturation depends on the activity coefficients and the ratio between actual and equilibrium concentration. The supersaturation, as it was explained, determines the nucleation rate and the growth rate.

Nucleation is the first stage of a phase change, where small areas of different phase are generated, called nuclei. For us, it is the creation of crystalline bodies within a supersaturated fluid. Most classifications distinguish between primary and secondary nucleation (J H Harker, 2013). Basically the difference between them is that primary nucleation occurs in the absence of crystals and secondary nucleation occurs in the presence of crystals. Primary nucleation is subclassified into homogeneous and heterogeneous. Nucleation rate depends on the diffusivity D_{AB}, the solubility c^*, the density c_c of the crystals and the supersaturation S (Mersmmann, 1999).

Crystal growth is an important stage of a crystallization process and consists in the addition of new atoms, ions or polymer strings. Growth rate, G, depends on the mass transfer coefficient, k_d, the dimensionless solubility c^*/c_c and the relative supersaturation, equation 2.40. Growth rate can be calculated then as:

$$G = \frac{\beta}{3\alpha} k_d \frac{\Delta c}{c_c} \tag{2.42}$$

Where α and β are the volume or surface shape factors, respectively.

e) Calcium to carbonate ratio [Ca^{2+}/CO_3^{2-}]

By adjusting the calcium to carbonate ratio has been proposed as one possible way to control the phase, morphology and physical properties of the precipitation process. Particularly [Ca^{2+}/CO_3^{2-}] ratio affects significantly to the polymorph selection (Özlem Cizer, 2012). Apparently stoichiometry between Ca^{2+} and CO_3^{2-} ions favors the presence of rhombohedral calcite. However, non-stoichiometric conditions ([Ca^{2+}/CO_3^{2-}] >> 1) favors the scalenohedral calcite formation under high pH. Scalenohedral is formed due to the excess of Ca^{2+} and OH^- ions present in the pore solution in contact with $Ca(OH)_2$ solid. The presence of OH^- ions dehydrates Ca^{2+} ions and this permits their adsorption at the calcite interface. The predominantly scalenohedral in crystal morphology due to the high [Ca^{2+}/CO_3^{2-}] ratio is also confirmed by Ukrainczyk et al. (Marko Ukrainczyk, 2007). They modified the conductivity of the process in order to check whether the [Ca^{2+}/CO_3^{2-}] ratio determines the transition between rhombohedral to scalenohedral calcite.

f) Carbon dioxide flow rate

Han et al. (Yong Sheng Han, 2005) studied the effect of flow rate and CO_2 content on the crystal morphology. In order to do that they precipitated the $CaCO_3$ introducing carbon dioxide mixed with nitrogen in a $CaCl_2$ solution. The carbon dioxide content in the mixed gas was 33.3 vol%. When the carbon dioxide flow rate was low, rhombohedral calcite was the predominant morphology and when

they increased the flow rate vaterite was the main component. But carbon dioxide content can also affect to the particle size.

Bang et al. (Jun-Hwan Bang, 2012) diluted $Ca(OH)_2$ with different concentrations and introducing gaseous CO_2 at different flow rates. They reported that the particle size decrease with a low CO_2 flow rate, although this effect is not significant in $Ca(OH)_2$ with more than 0.1 M. As the particle size smaller, this permits to enhance CO_2 dispersion.

g) Conductivity

It has been demonstrated in a study made by Ukrainczyk et al. (Marko Ukrainczyk, 2007) that the specific surface area depends on temperature and conductivity. The higher conductivity in the process, the bigger is the specific surface area, but in the case of the temperature only if it decreases the specific surface area increases. They explained this phenomenon as the effect of temperature on the concentration of dissolved electrolytes that produces a change in conductivity. When high concentration of $Ca(OH)_2$ is dissolved, that means an increase in conductivity, the CO_2 solubility is enhanced at high pH.

h) Stirring rate

In the same study commented in the previous section, (Marko Ukrainczyk, 2007), stirring rate, conductivity and gas flow rate have been studied as the most important factors for CO_2 conversion to calcium carbonate. At high values of stirring rates and conductivity it was possible to obtain the maximum CO_2 conversion to calcium carbonate.

i) Carbon dioxide bubble size

Reducing the bubble size of the carbon dioxide gas is a promising way to improve the efficiency of carbon dioxide consumption and to reduce particle calcium carbonate particles. Jung et al. (Jun-Hwan Bang, 2012) studied the effect of microbubbles, bubbles smaller than 50 μm, in calcium carbonate precipitation process. In their study, thanks to their technic using microbubbles less $Ca(OH)_2$ was necessary to obtain the same specific surface area as in other experiment using a bubble column. They demonstrated that using carbon dioxide microbubbles decreased the particle size of the PCC.

j) Additives

The presence of additives in the precipitation process can promote the absorption of carbon dioxide into aqueous solution, is able to adjust the pH making it higher and it can control the crystal phases and morphologies of precipitated calcium carbonate (Wittaya Chuajiw, 2014). Particularly, in order to control the crystal morphology, it has been studied organic additives such as bio-macromolecules, synthetic macromolecules and synthetic low molecular weight compounds. In that study it was demonstrated that only the stable phase, calcite, was formed without additives. On the other hand, vaterite and aragonite were formed by adding of organic amine and amino-acid molecules. Regarding inorganic additives, Tai et al. (Clifford Y. Tai, 1998) studied the effect of the $MgCl_2$, $MnCl_2$ and KH_2PO_4. They noticed that $MgCl_2$ and $MnCl_2$ favor the formation of aragonite and calcite depending on other conditions and KH_2PO_4 in all the cases favors calcite formation. Xiang et al. (L. Xiang, 2002) studied how $MgCl_2$, $ZnCl_2$ and $C_{10}H_{16}N_2O_8$ (EDTA) influence in the particle size. EDTA was

found to be the best one to reduce the particle size from 75 to 50 nm. Their crystal morphology in all their experiments that they obtained was vaterite. They could reduce the partice size because when they added EDTA the carbonation time was reduced from 80 to 40 min and the faster carbonation process permits to form super-fine particles. When $ZnCl_2$ was added particle size was decreased as well, they obtained vaterite crystals with about 0.2 μm diameter. The effect of $MgCl_2$ was not as significant as $ZnCl_2$ and EDTA.

3. Experimental Work

As the aim of the thesis is to try to produce the scalenohedral form of calcite, it was decided to do several tests varying the solvent concentration. The selected solvent concentration was 0.01 M. It was attempted with this concentration because it was wanted to simulate the conditions under which Hannu-Petteri Mattila from Åbo Academy produced scalenohedral PCC. Mattila achieved this crystal morphology with 0.01 M of ammonium chloride at 45°C in laboratory scale.

As Hannu-Petteri was successful under those conditions we decided to reproduce them. Apart from all mentioned above, he obtained scalenohedral calcite maintaining the pH and the temperature constant. Before planning the experimental work in the pilot scale we took all of those conditions into account. However, to maintain the pH and the temperature constant in the pilot scale is more challenging than in the laboratory scale. For example, the pH-meter in the carbonation reactor is situated 45 centimeters from the bottom of the reactor and this means that, in order to measure the pH all the time, the reactor has always to have solution above that level. Additionally it is also difficult to maintain the temperature at 45°C all the time as the size of the reactor is larger: 5 liters reactor in the laboratory scale and 200 liters in the pilot scale.

The first one of the tests was in the pilot-scale Slag2PCC Plant. Then some tests were taken in the laboratory-scale because it was wanted to set correctly the conditions in the laboratory in order to produce the scalenohedral PCC and with the first test it was not achieved that. Thereby, it was possible to save time and resources for following tests. Once it was known the parameters to modify, the rest of the tests were done in the pilot-scale plant. Test results and a further analysis of them are shown after explanation of the equipment setup and procedure in both laboratories.

3.1 Pilot-Scale Experimental Work

3.1.1 Equipment Setup

On the figure 3.1 is showed the Slag2PCC demonstration plant. As it can be seen, there are three reactors, all of them with 200 liters. The first one is the extraction reactor and the others are the carbonation reactors. In the extraction reactor, the slag is feed from the top and the ammonium chloride is bumped from the fresh solvent tank or from the recycled solvent tank. Then the steel slag is mixed with the ammonium chloride with the help of a mixer. In this reactor the calcium of the solution is extracted from the steel slag. Afterwards it is necessary to filter the solution in order to separate efficiently the solid slag particles, this is done by one of the extraction filters, which both have 1 µm pore size. Then the solution is filtered again by the quantitative filter 1, which is formed by two other filters with 1µm and another one with 0.45 µm placed in series to separate the slag and the produced PCC from the liquid stream. After these two filtrations, the solution can either lead to the storage tank 1 (200L) or to one of the carbonation reactors. Preferably most of the solution is brought to the reactor 2, and then, the rest of the solution is brought to the reactor 3 with a splitter. Later the carbonation takes place in the carbonation reactor, the calcium rich solution is bubbled with the carbon dioxide. When it is completed, the resulting liquid is filtered in the same way as in the extraction step. Finally, the solvent is stored in the solvent tank 1 or 2 in order to recycle the solvent.

In each reactor, temperature and pH can be measured and there is also a three-level 2-bladed variable speed drive agitator, with a maximum speed of 202 rpm in the extraction reactor and 170 rpm for the carbonation reactors. Furthermore, the pilot-plant has also two heat exchangers to heat or cool the liquid in all the reactors. Heat exchangers work with hot or cold water and the maximum temperature depends on the season, in winter is 80 ºC but in summer is only 60 ºC. The two carbonation reactors have spargers of 1mm at their bases and the carbonating flow from the carbon dioxide bottles to these reactors is set with a rotameter.

In the figure 3.1 a picture of the three reactors is shown in more detail:

Figure 3.1: Pilot Plant reactors

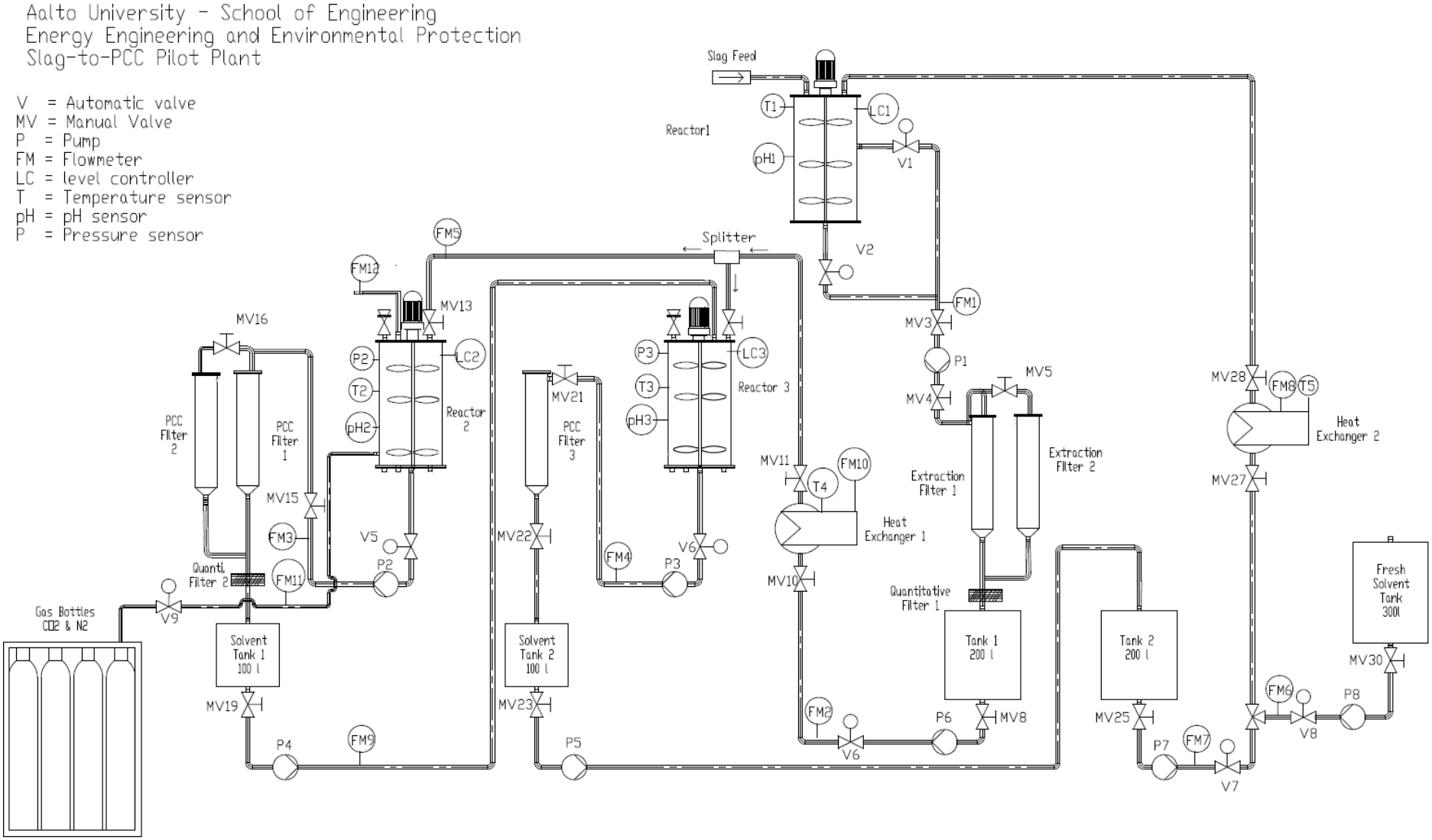

Figure 3.2: Slag-to-PCC Pilot Plant

3.1.2 Experimental Procedure

Each time before conducting extractions tests the low concentration ammonium chloride was prepared introducing 84 grams of solid NH_4Cl in 170 L of water and it was mixed everything with a manual agitator until it was dissolved. When the aqueous ammonia chloride was ready the solvent was pumped from the fresh solvent tank or from the recycled solvent tank. Then we weighed the slag and introduced it in one time from the top of the reactor. While introducing the slag into the reactor it was mixed everything with the agitator at 202 rpm. After that extraction took place during 45 minutes. When extraction was completed, the solution was filtered through one of the PCC filters situated below the extraction reactor and the calcium-rich solution was stored in the tank 1.

In order to realize the carbonation tests the Ca-rich solution was pumped from the tank 1 to the carbonation reactor (reactor 2). Solution was pumped to the carbonation reactor and then the carbonation reaction took place adding carbon dioxide and mixing everything at 170 rpm. The same carbon dioxide flow was not used in all the tests, it was possible to modify it using a rotameter and not all the carbonation reactions occurred at the same time. During carbonation the pH and the temperature were recorded each ten seconds. To obtain 45 ºC in the carbonation process the solution was heated with the help of the heat exchanger 1, in which hot water was introduced.

In some tests it was taken samples after carbonation process and sometimes during carbonation process to study the crystal morphology and how parameters like carbon dioxide flow or incoming or outgoing flow solution affect it. In order to do that it was necessary to wait until the PCC was in the bottom of the glass and then the glass was introduced in an oven at high temperature for hours. When the PCC was dried, it was sent it to the laboratory to realize the SEM images.

Extraction tests

The steel slag used in the pilot-scale Slag2PCC Plant was provided by SSAB- Ruukki in Raahe, Finland. This steel slag is optimal for the process due to its high free lime content, in this case the content of CaO is 51.40% of the total chemical composition. Below is shown the overall components in the steel slag used:

CaO	FeO	SiO_2	MnO	Al_2O_3	MgO_2	V_2O_3	Ti	P	Cr	Na_2O
51.4	14.60	13.70	1.80	1.60	1.50	2.05	0.55	0.45	0.25	0.1

Table 3-1: XRF analysis of steel converter slag (> = 0.1 wt-%)

The grain size of the steel slag used was 250 µm. The tests were conducted with low concentration (0,01 M) of ammonia chloride. After extraction process the calcium extraction efficiency was calculated. In order to do that the solution was analyzed with ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy). This technique is widely used in chemistry for metal traces detection. It is a kind of emission spectroscopy that consists of the utilization of inductively coupled plasma to produce excited atoms and ions that are going to emit electromagnetic radiation at wavelengths characteristic of certain elements. When the electrons return to the ground state this produces the emission of photons of light. The spectrometer disperses the light and the more the intense is the light, the more concentration of an element has the sample. The results with this technique depend on the extraction conditions such as extracting solution composition, pH and temperature (R. Traversi, 2014).

In total, five extraction tests were realized. It was decided to set the same extraction conditions and to not modify them since the optimal extraction conditions for producing scalenohedral PCC have been fixed before. The initial conditions for the tests were:

Extraction			
Slag (kg)	Solvent (L)	[NH4Cl] (M)	SLR (g/L)
17	170	0,01	100

Table 3-2: Initial conditions for tests

The amount of slag and solvent used were specifically those values in order to obtain a solid to liquid ratio (SLR) of 100 g/L:

$$SLR = \frac{m_{slag}\,(g)}{V_{solvent}(l)} = \frac{17000}{170} = 100\ g/l \tag{3.1}$$

It was decided to have 100 g/L of SLR, despite the fact that with high SLR less extraction efficiency is obtained according to Said et al. (Arshe Said, 2013). Theoretically to have a SLR of 100 g/L instead of 50 g/L should lead to obtain a higher [Ca^{2+}] and thus, to a higher extraction efficiency. Given these conditions, it was decided to try with 100 g/L to verify if the theory was correct.

Carbonation tests

In carbonation tests it can be seen that there is a discrepancy between the liters of solvent used for the extraction tests and the liters of solution used for carbonation tests. This is because after filtration of the Calcium-rich solution some of it remains in the slag. Furthermore, when the carbonation tests were performed it was decided not to fill completely the reactor because it would have been more difficult to produce scalenohedral PCC. The temperature was set at 45 ºC (as it was the one at scalenohedral PCC was obtained) and the agitation for all the tests was the maximum speed, 170 rpm. The carbon dioxide in the first two tests was 14 L/min and later on it was noticed that it was too much flow if scalenohedral PCC was wanted to be produced. After an overview of Hannu-Petteri's test parameters it was set correctly the parameters for following tests. After those tests it was tried with 4 L/min of CO_2 flow but it was still too high and then it was tried with 1 L/min and 0.5 L/min. All these parameters are summarized in the table below.

Carbonation					
Solution (L)	Temperature (°C)	V_{gas} (CO_2) (L/min)	Agitation (rpm)	$V_{liquid,in}$ (L/min)	$V_{liquid,out}$ (L/min)
106	45	14	170	12.73	13.34
108	45	14	170	18.63	18
114	45	4	170	18.59	17.96
114	45	1	170	18.58	18.15
112	45	0.5	170	18.59	17.93

Table 3-3: Parameters in carbonation tests

3.1.3. Results and discussion

In the extraction tests the maximum calcium extraction efficiency obtained was 4% as Table 3.3 shows. This result was obtained performing analysis with the ICP-AES technique at room temperature. This could be due to the low concentration of the solvent. The maximum calcium extracted was obtained 30 minutes after starting the precipitation.

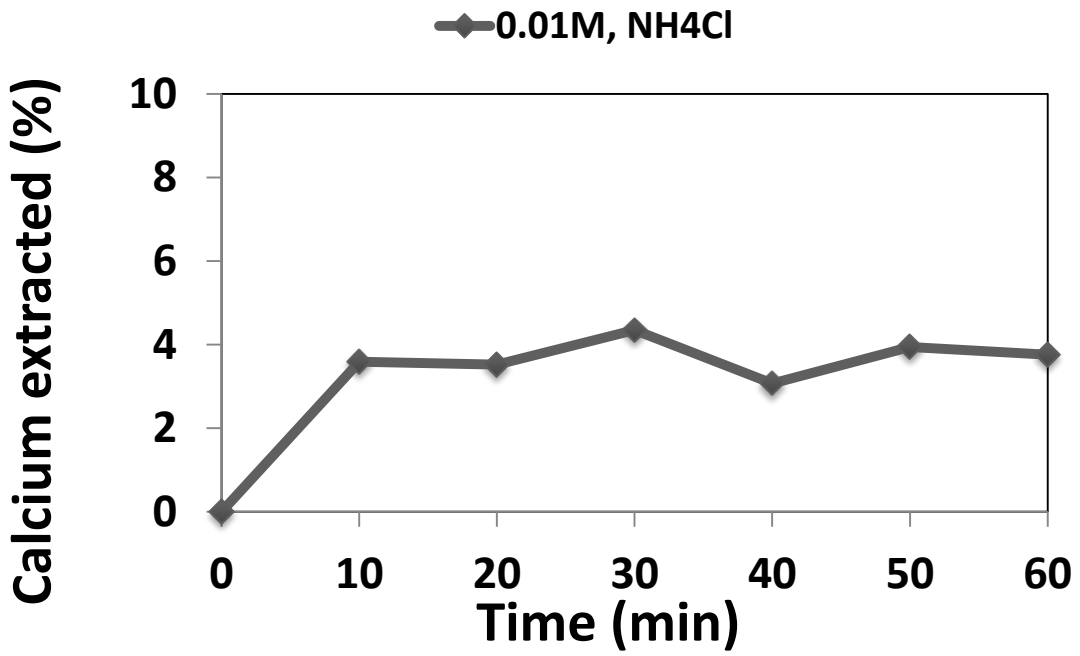

Figure 3.3: Results for calcium extraction efficiency

The following figures show the pH and the temperature during the carbonation tests. It can be seen that the pH in the first test is almost acid, this might be because the calcium-rich solution was stored more time than in the other tests. Both temperature and pH were tried to maintain constant in all the tests, but the temperature was more difficult to maintain. The duration of the tests are different basically because of the carbon dioxide flow. Normally the less carbon dioxide flow introduced in the reactor, the more time needs the precipitation to take place, except in the test three (figure 3.6) that the duration was only ten minutes. This could be due to a bad performing of the test.

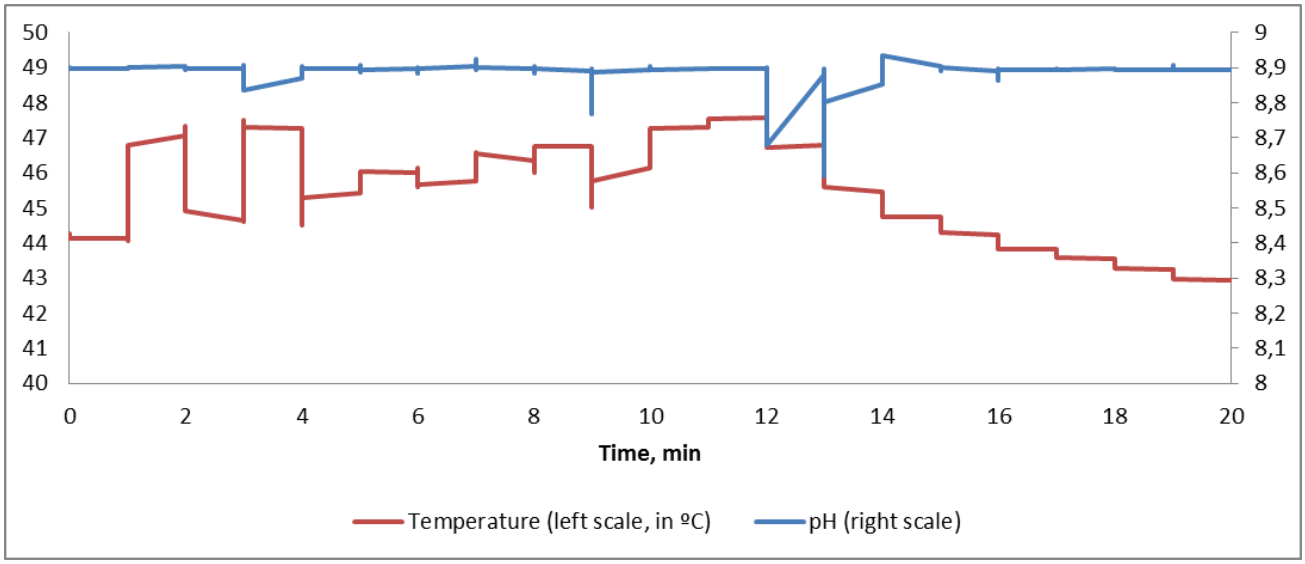

Figure 3.4: Temperature and pH registered in test 1 pilot scale

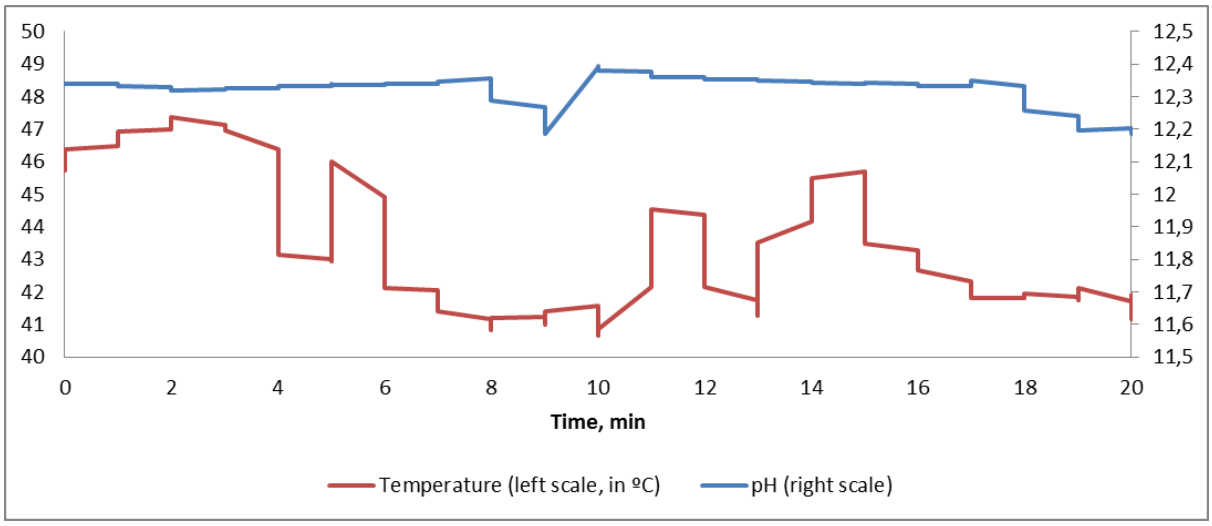

Figure 3.5: Temperature and pH registered in test 2 pilot scale

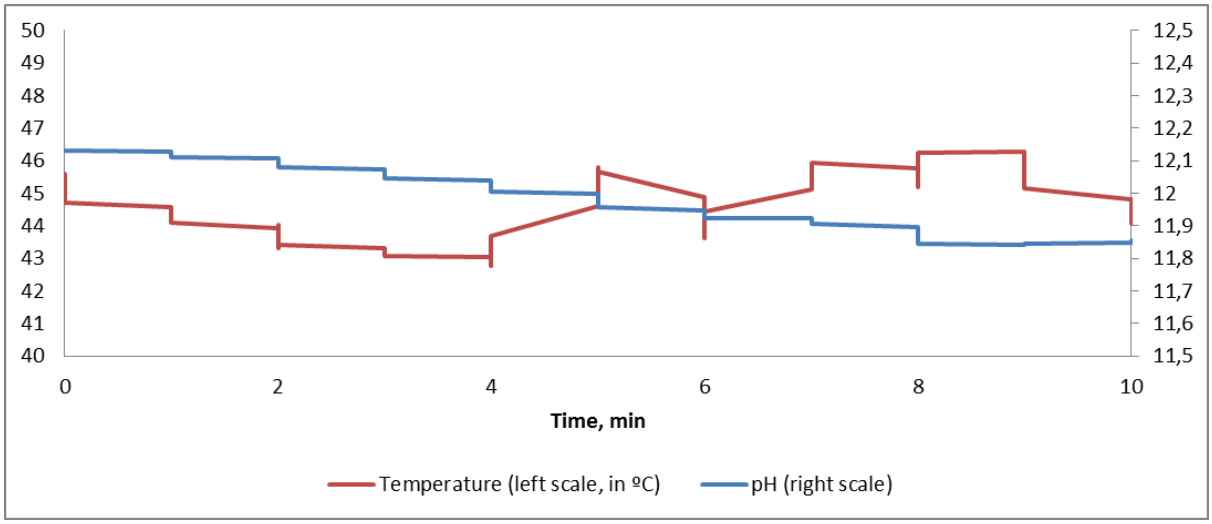

Figure 3.6: Temperature and pH registered in test 3 pilot scale

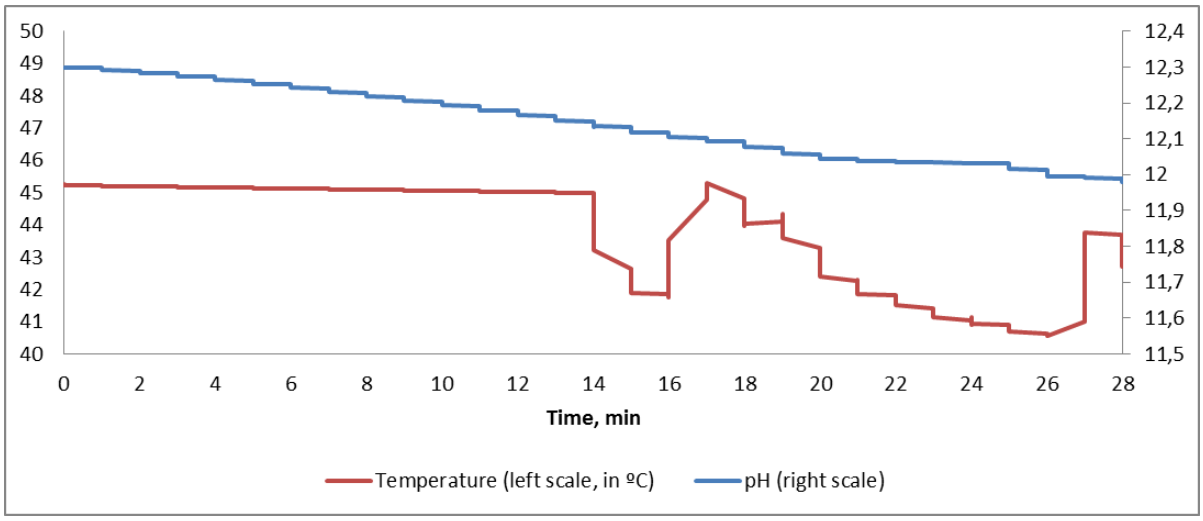

Figure 3.7: Temperature and pH registered in test 4 pilot scale

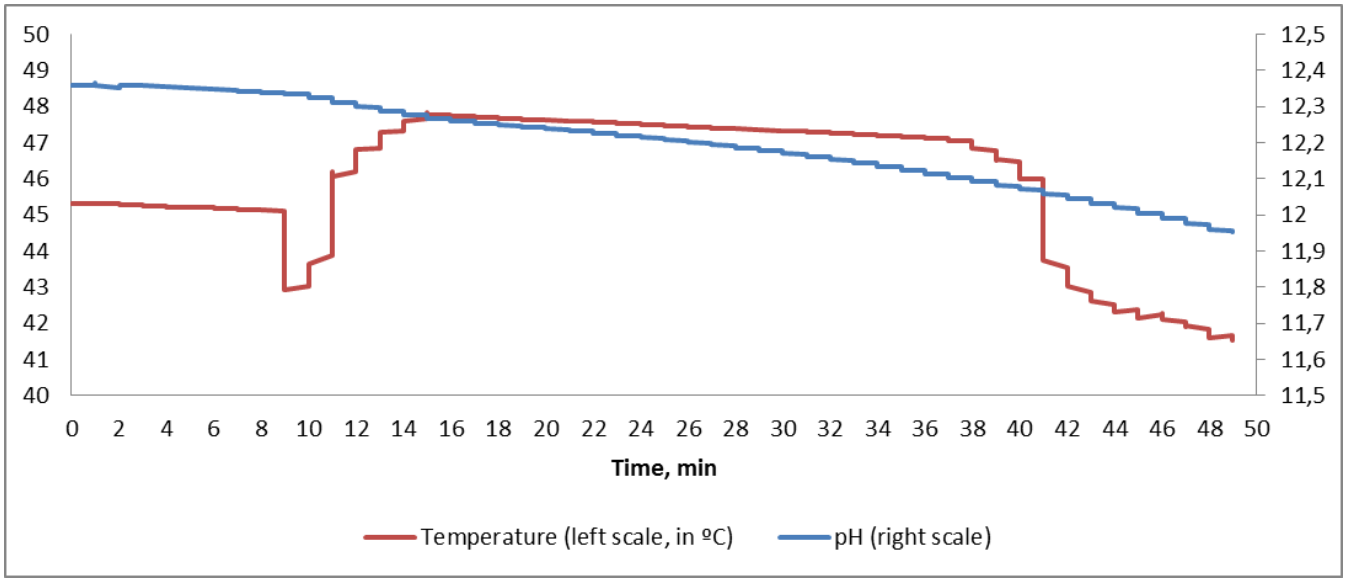

Figure 3.8: Temperature and pH registered in test 5 pilot scale

After carbonation took places, the final product was analyzed in a laboratory and SEM Images were taken. Although the aim was to obtain scalenohedral calcite, it was not achieved that completely. The first test is clearly rhombohedral calcite due to a pH more acid than in the other tests. The second test could be a mixture of aragonite (because of the needles) and an attempt of scalenohedral calcite. The third test was not successful either, it is basically rhombohedral calcite with some needles. The fourth test was slightly better than the previous one, with more attempts to scalenohedral calcite and less rhombohedral calcite. The fifth test may be the best one: there is no rhombohedral calcite and mostly star shapes indicating the presence of what I would say scalenohedral. This is due to the use of carbon dioxide, the flow it was used only 0.5 L/min in that one. This was set to replicate Hannu Petteri-Mattila's conditions: with 10 L of solution he used 0.05 L/min of carbon dioxide so for 0.5 L/min made sense for 112 L.

It can be appreciated in the figure 3.9 that the final product is not very homogeneous, this is because during the process the solution was not mixed so fast. In the pilot plant it could only be reached 170 rpm of rotation speed, so this cannot be improved.

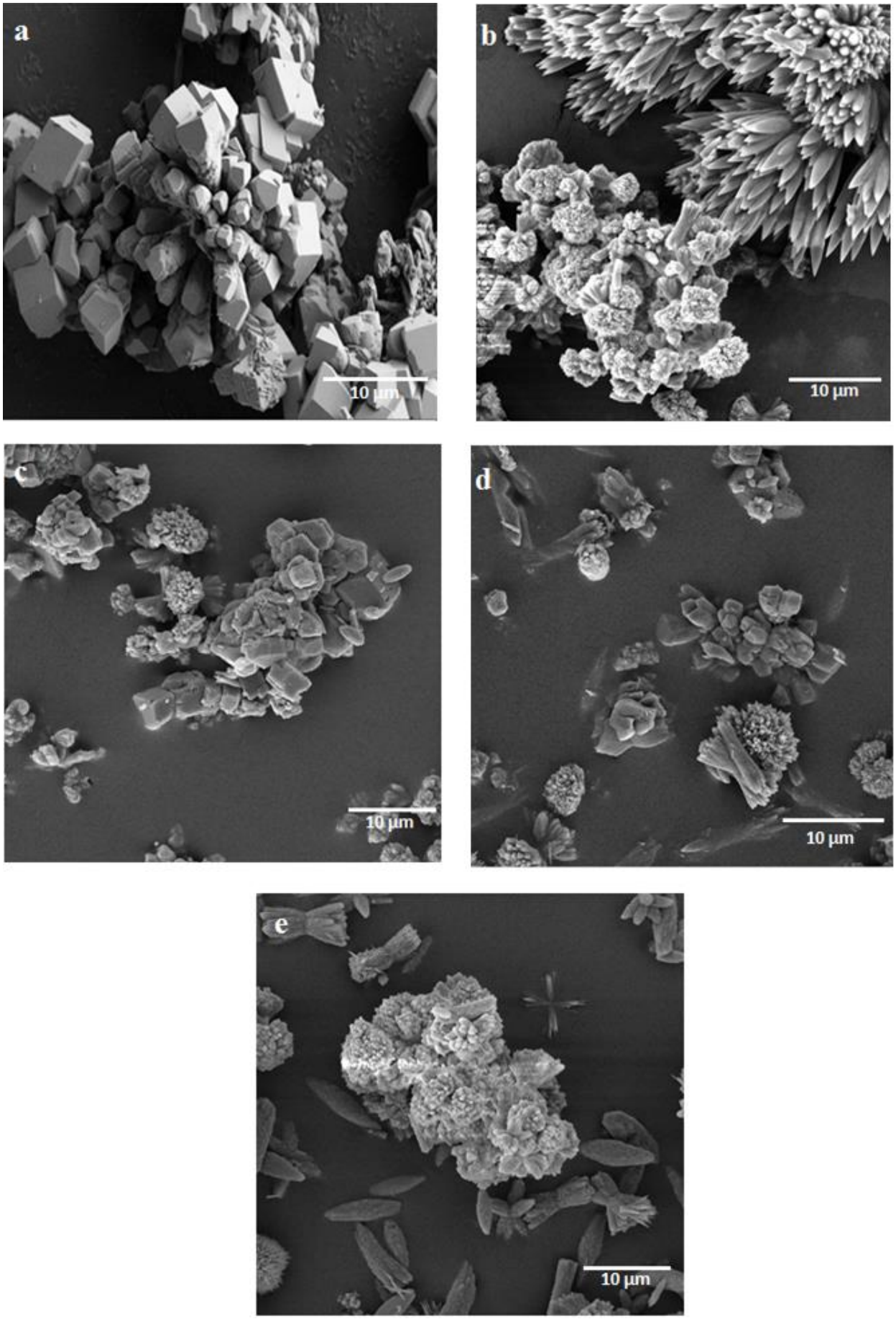

Figure 3.9: SEM images from pilot plant tests. a) Test 1 1500x, b) Test 2 5000x, c) Test 3 6670x, d) Test 4 6670x, e) Test 5 5000x

3.2. Laboratory-Scale Experimental Work

During the first tests performed in the pilot plant it was noticed that scalenohedral form of calcite was not achieved, only rhombohedral calcite was obtained. It was decided then to perform some carbonation tests in laboratory scale to set correctly the conditions for the pilot-scale. It was tried to reproduce the conditions under Hannu-Petteri Mattila obtained scalenohedral calcite: all of the tests took place at 45°C with 0,01 M NH_4Cl and trying to maintain pH and temperature constant. Four tests were done in laboratory scale under different conditions: stopping the carbon dioxide flow when the pH was too low, with or without incoming and outgoing flow solution, etc. All the conditions are going to be analyzed later.

3.2.1 Equipment Setup

The equipment used in the laboratory consists of a jacketed reactor of 5 liters, a water bath that allows heating up the solution at the desired temperature, a pH-meter, a temperature sensor, an agitator, a carbon dioxide supplier and a pump. Furthermore, in our experiments it was arranged a system to put solution in and to take it off. This can be better seen in the figure 3.10, in which a photo of the equipment is shown.

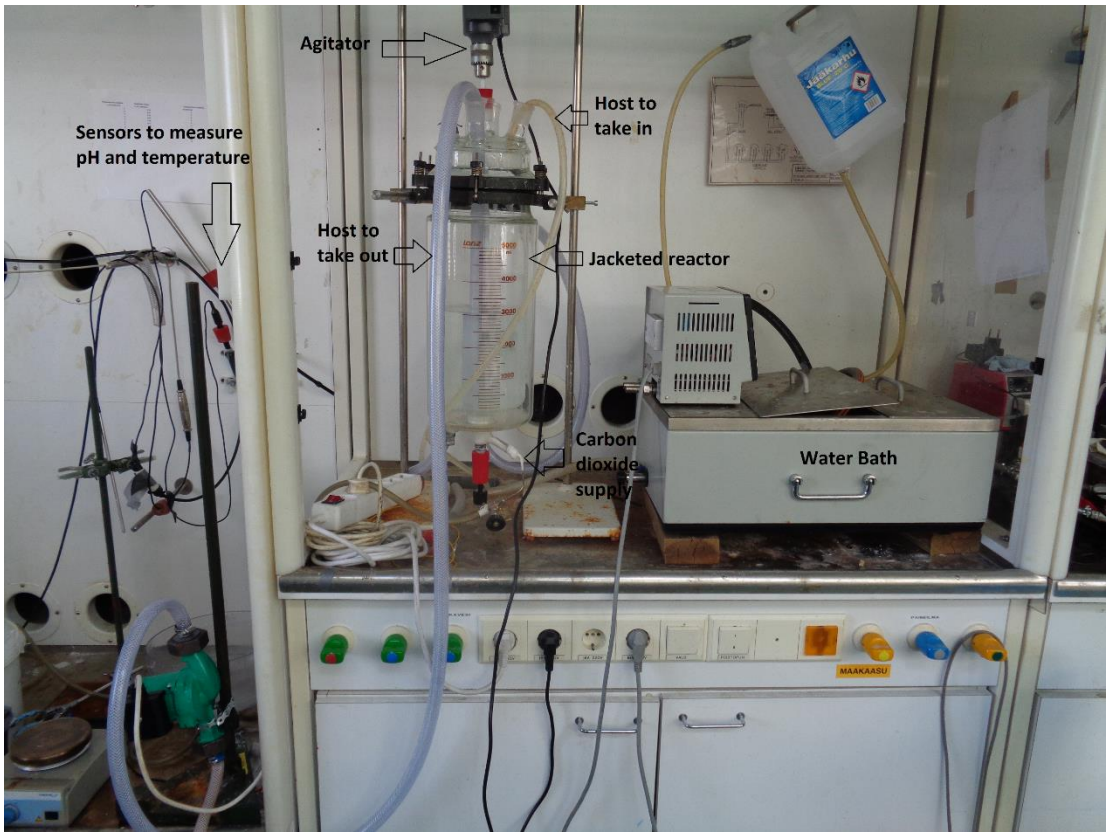

Figure 3.10: Laboratory equipment

3.2.2 Experimental procedure

The calcium-rich solution used in the laboratory scale was taken from the pilot plant after extraction tests. As it was desired the temperature of the carbonation to be 45 °C first it was introduced the prepared solution in the water bath until the solution was hot enough. Then the solution was pumped to the jacketed reactor until it was reached 4 liters. After that carbon dioxide was introduced through the CO_2 supplier previously set as in the pilot-scale with a rotameter and everything was mixed all the time with the agitator at 427 rpm. The pH and the temperature were also recorded each ten seconds.

In each test conditions were modified such as carbon dioxide flow and incoming and outgoing solution. Modifications were the ones as follows:

- In the first test carbon dioxide flow was set at 0.2 L/min and it was taken off solution approximately at double speed it was introduced solution.
- In the second test it was decided to not have incoming and outgoing solution to study the effect in the crystal morphology, the solution was maintained all the time in the reactor. The pH was controlled introducing carbon dioxide: when the pH was too low, it was closed the CO_2 and when the pH increased, it was again introduced carbon dioxide. The gas flow, the solution volume and the temperature were the same as in the previous test.
- In the third one carbon dioxide was set to the half flow as previous tests, 0.1 L/min and it was noticed that the liquid flow rate was too fast and it was decided to decrease it. In order to do that, a smaller host was introduced inside and thanks to that we reduced the incoming flow rate from 2.4 l/min to 1.09 l/min. To control the outgoing flow, the tap opening degree was modified until a flow of 0.42 l/min was obtained, half of the incoming flow. Two minutes after it was started the carbonation, the precipitation took place and carbon dioxide was introduced. When the precipitation took place the process of introducing and taking out solution also started, not before. When the pH was too low, carbon dioxide was closed and when it rose it was opened again. In particular, when the pH was approximately 11.85 it was closed the carbon dioxide and when it was 11.88 it was opened the gas again, in total it was done twice.
- In the fourth test it was decided to change the number of times the carbon dioxide was stopped in order to maintain the pH more constant. Instead of closing the carbon dioxide when the pH was about 11.85 it was decided to close it when the pH was approximately 11.95. So, in this test it was finally closed the carbon dioxide flow five times.

Once we finished the tests reactor was emptied and some solution was put in a glass. Once the solution was settled, it was removed some liquid and it was put in a glass inside an oven at high temperature in order to dry the PCC. When the sample was dried it was sent them to the laboratory to obtain the SEM images. To clean the reactor, it was mixed hydrochloric acid with water to remove all possible calcium carbonate particles remaining.

3.2.3 Results and discussion

The conditions for the extraction tests were the same as in the pilot scale as for the carbonation tests in the laboratory it was used the calcium-rich solution obtained in the pilot plant. In the table 3.4 are summarized the conditions mentioned in the previous chapter and the average pH obtained in each test.

	Rotation speed (rpm)	Average pH	Solution (L)	Temperature (°C)	$V_{liquid,in}$ (L/min)	$V_{liquid,out}$ (L/min)	V_{gas} (L/min)
Test 1	427	11.86	4	45	2.4	4.28	0.2
Test 2	427	11.88	4	45	-	-	0.2
Test 3	427	11.91	4	45	1.09	0.42	0.1
Test 4	427	11.91	4	45	1.09	0.42	0.1

Table 3-4: Parameters in carbonation tests (laboratory scale)

The figures from 3.11 to 3.14 show the pH and the temperature recorded for each test. As it was already known, the pH and the temperature were much easier to control in the laboratory scale due to, basically, the amount of liters of solution involved in the process were 4 and in the pilot plant were more than 100. So, as predicted, in general the temperature remained constant. To control the pH, the technique mentioned in the previous chapter was used.

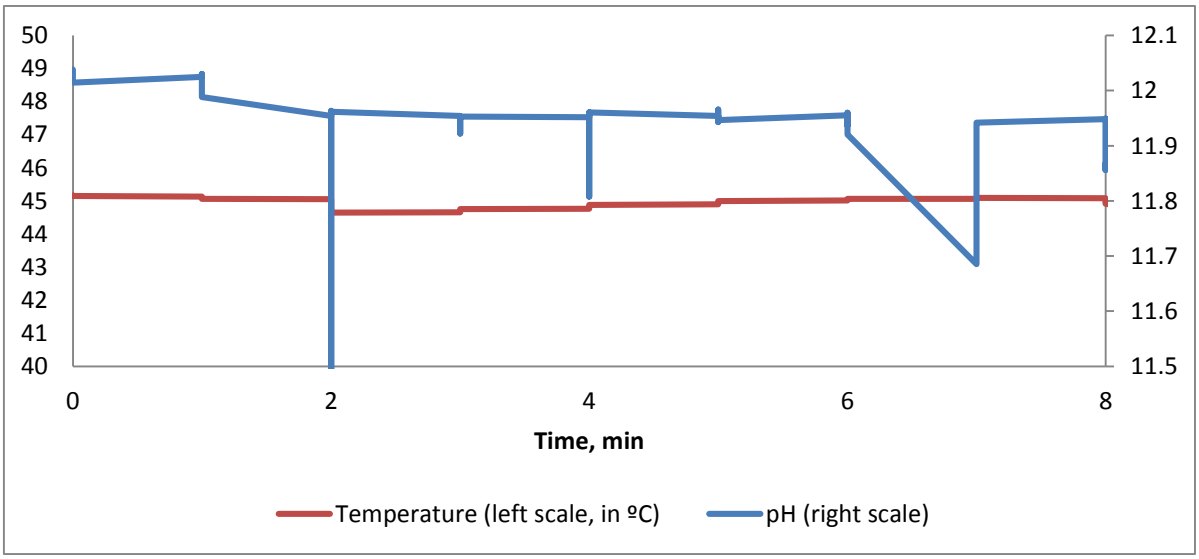

Figure 3.11: Temperature and pH registered in test 1 laboratory scale

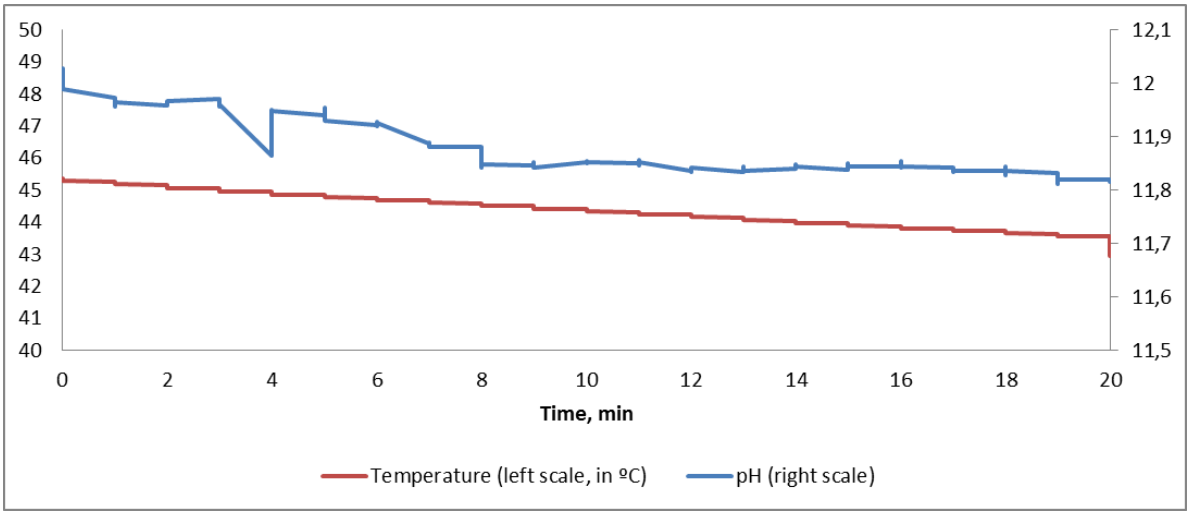

Figure 3.12: Temperature and pH registered in test 2 laboratory scale

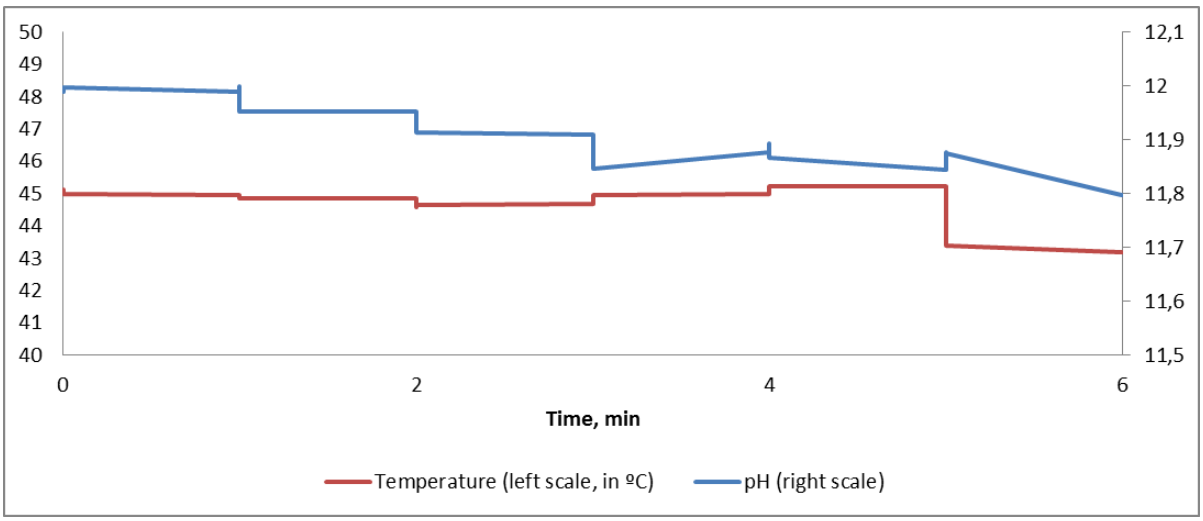

Figure 3.13: Temperature and pH registered in test 3 laboratory scale

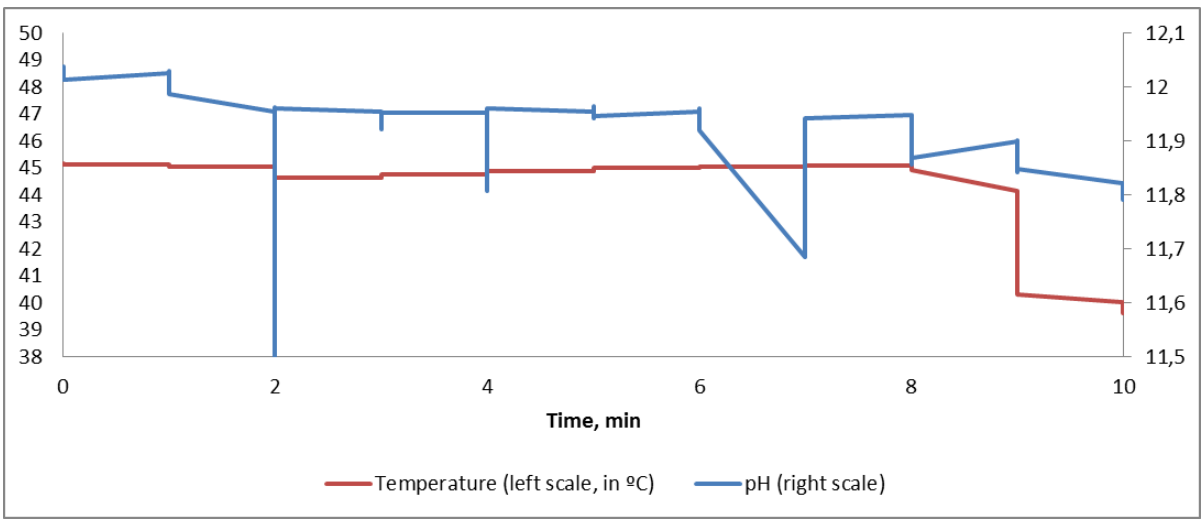

Figure 3.14: Temperature and pH registered in test 4 laboratory scale

SEM images obtained were in general satisfactory, the final product was homogeneous thanks to the higher speed of the mixer than in the pilot scale. Furthermore, the crystal morphology seems to be close to scalenohedral, although in the case of the first two tests (figure 3.15 a and b), it looks like traces of vaterite because of the needle shapes. Nevertheless, in the third test (figure 3.15c), star shapes seem to start forming. It was clearly the most successful of the tests in the laboratory scale, and we adapted the parameters from this test to the tests in the pilot plant.

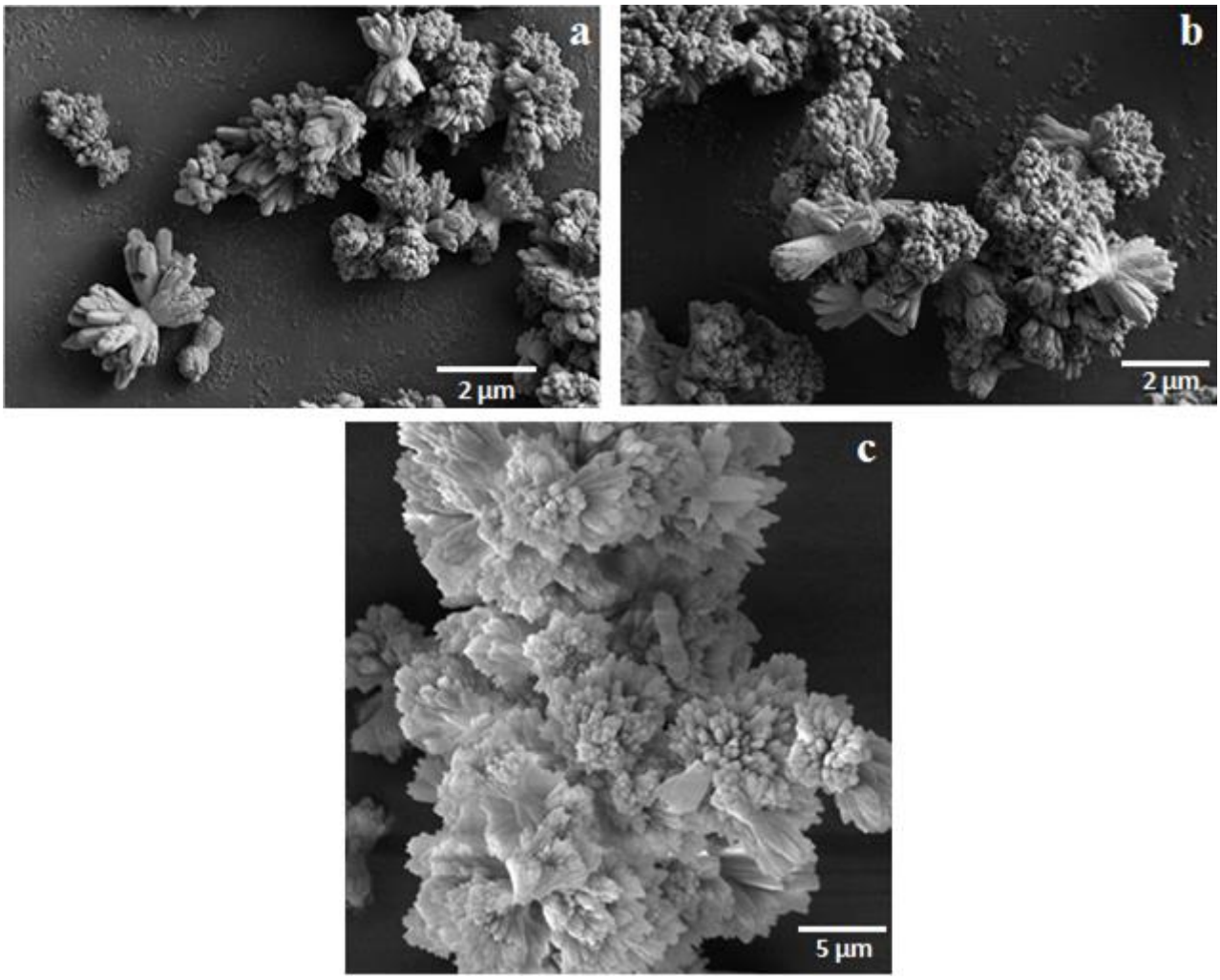

Figure 3.15: SEM Images from laboratory scale tests a) Test 1 2600x, b) Test 2 5000x, c) Test 3 10000x

4. ECONOMIC CALCULATIONS

In this chapter economic calculations have been made in order to find out if producing PCC is a profitable process. The parameters used for this calculations were the ones used in the fifth pilot plant test:

Extraction			
Slag (kg)	**Solvent (L)**	**[NH4Cl] (M)**	**Duration (min)**
17	170	0.01	40

Table 4-1 Extraction parameters used in economic calculations

Carbonation				
Solution (L)	**Temperature (°C)**	**$V_{gas}(CO_2)$ (L/min)**	**V_{liquid} (average) (L/min)**	**Duration (min)**
112	45	0.5	18.3	50

Table 4-2 Carbonation parameters used in economic calculations

In order to estimate the costs, the calculations shown below were done:

1) Cost of water heating. It was calculated the price of the energy needed to heat up the water used in the heat exchangers. I used the formula of the heat:

$$Q = m\ Cp\ \Delta T$$

Where Q is the heat in KJ used in the process, m is the mass in kg of the water utilized, Cp is the specific heat capacity in $\frac{kJ}{kg\ ^{o}C}$ and ΔT is the increment of the temperature. Then the calculation is:

$$Q = m\ Cp\ \Delta T = 200 * 4.18 * (45 - 15) = 25080\ kJ$$

The quantity of the mass used was estimated as 200 L for the duration of the carbonation (50 min). The initial temperature of the water was estimated as 15 ºC and the temperature that it is wanted to reach is 45ºC. Then the calculation of the price of the energy used was calculated as follows:

$$Price\ of\ heating\ the\ water = \frac{25080\ kWs}{50 * 60\ s} * 0.072\ \frac{€}{kWh} = 0.50€$$

The price electricity in Finland for industry in 2014 was 0.072 €/kWh (Anon., 2015).

2) Cost of pumping the solution to the extraction reactor and to the carbonation reactor:
   a. *Cost of pumping the solution to the extraction reactor*:

The time needed to pump 170 L of solution with an average flow of 18.3 l/min is 9.3 min (170/18.3 = 9.28 ~9.3 min). Then the price of pumping this amount of solution is:

$$Price\ of\ pumping\ solution\ to\ the\ ext\ reactor = 250\ W * \frac{1\ KW}{1000\ W} * 9.3\ min\ \frac{1\ min}{60\ s} * 0.072\ \frac{€}{kWh} = 0.0028\ €$$

The power draw of the pump is 250 W.

b. *Cost of pumping the solution to the carbonation reactor*:

The time needed to pump 112 L of solution with an average flow of 18.3 l/min is 6.1 min (112/18.3 = 6.1 min). Then the price of pumping this amount of solution is:

$$Price\ of\ pumping\ solution\ to\ the\ ext\ reactor = 250\ W * \frac{1\ KW}{1000\ W} * 6.1\ min\ \frac{1\ min}{60\ s} * 0.072\ \frac{€}{kWh} = 0.0018\ €$$

3) Cost of mixing the solution in the extraction reactor and in the carbonation reactor:

a. *Cost of mixing the solution in the extraction reactor*:

The time for the extraction in this case is 40 min and the power draw of the agitator is 370 W. The price then is the one as follows$Price\ of\ mixing\ extraction\ solution = 370\ W * \frac{1\ KW}{1000\ W} * 40\ min\ \frac{1\ min}{60\ s} * 0.072\ \frac{€}{kWh} = 0.018\ €$

b. *Cost of mixing the solution in the carbonation reactor*:

The time for the extraction in this case is 50 min. The price then is the one as follows:

$$Price\ of\ mixing\ carbonation\ olution = 370\ W * \frac{1\ KW}{1000\ W} * 50\ min\ \frac{1\ min}{60\ s} * 0.072\ \frac{€}{kWh} = 0.022\ €$$

4) Cost of purchasing slag

Cost of purchasing the steel slag was estimated to 8.48 €/ton as in the pilot plant steel is not produced. This is because according to European Comission (N. Pardo, 2012) the price for electric furnace slag was 8 €/ton in 2010. So, with an annual growth rate of 1.2 % in 2015 a ton of slag would be 8.48€. Then for our process with 17 kg of slag the price would be 0.144 €

5) Cost of purchasing solid NH_4Cl

Cost of purchasing solid NH_4Cl was found to be 11.95 $ for 500 g (company, 2016). In euros this would be approximately 10.67 €. Then, for 84 g of slag (which is the amount utilized in each process to obtain liquid ammonium chloride) the price would be 1.79 €.

Cost concepts	**Costs (€)**
Slag purchasing	0.144
Solid ammonium chloride purchasing	1.79
Cost of electricity for mixing in both process	0.018 + 0.022 = 0.04
Cost of electricity for pumpin in both process	0.0018 + 0.0028 = 0.0046
Cost of electricity for heating water in carbonation	0.50
Total	2.4786 ~ 2.5

Table 4-3: Economic calculations to study slag2PCC feasibility

Several assumptions have been made in order to do an approximate cost calculation. The cost of grinding the slag is not considered as it was given to us with a particle size of 250 µm. As the company who provided the slag, Ruukki, is in Helsinki the cost of transportation of the slag is not considered, nor the transportation of the PCC. Heat losses are also not considered.

The production for 17 kg of slag of PCC is estimated to produce 4.26 kg. This is because with the slag using 0.01 M NH_4Cl and 100 g/l the extraction efficiency is 25.05%. Thus, the price for the PCC for our process would be approximately:

$$Price\ for\ PCC = \frac{2.4786\ €}{0.00426\ ton\ PCC} = 581.83 \frac{€}{ton\ PCC}$$

In a previous chapter it was mentioned that the PCC price can reach about 400-500 €/ton PCC. This purchasing price is for big companies, and as our process could be considered more or less as a large scale due to the size of the reactors, the price is more or less the expected.

5. CONCLUSIONS

This thesis has focused on the parameters that have to be taken into account in order to obtain scalenohedral form of calcite. This crystal morphology is an interesting research topic due to the fact that the process of obtaining scalenohedral PCC, apart from producing a valuable product for several industries, permits the capture and storage of carbon dioxide. Furthermore, an approximate calculation of producing the PCC has been made.

The most important parameters that affect crystal morphology are pH, carbon dioxide flow, temperature and solvent concentration. Temperature and pH were recorded during tests in the pilot plant and in the laboratory and carbon dioxide flow was modified as desired. From previous research that demonstrated optimal temperature to produce scalenohedral PCC, it was wanted to be constant at 45ºC. Same research also demonstrated that there were more chances to produce this crystal if the solvent had low concentration, so all tests performed were done with low solvent concentration, 0.01 M.

Once all tests were finished it was noticed that best attempts to produce scalenohedral PCC were the ones with low carbon dioxide flow. The best result was in the laboratory scale when using 0.1 l/min of carbon dioxide flow. Results in the pilot plant were not as good as the one mentioned. This might be due to that the final product was not completely homogeneous, directly related to the agitation speed of the mixer. Rotation speed in the pilot plant was at maximum 170 rpm and in the laboratory scale was 427 rpm. Higher speed is not possible in the pilot plant at the moment, although it might be an interesting factor to modify if homogenous scalenohedral PCC is wanted to be produced in the pilot plant.

From an economical point of view, the slag2PCC process should be improved with such a small concentration of solvent in order to obtain a better profit. It has to be taken into account that certain parameters were not considered in the economic calculation such as transport and heat losses but it permits to see that there might be good potential in producing it.

From an environmental point of view, it was possible to appreciate that the best attempts to produce scalenohedral PCC were the ones in which low carbon dioxide flow was used. Despite that it is still one good way in order to capture and storage carbon dioxide.

Finally, after an overview of the utilization of PCC in the plastic and pharmaceutical industry it can be affirmed that it is not widely used in these industries, even less for pharmaceutical products. This might be due to the fact that the advantages of using PCC are not offset by the cost of purchasing it.

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